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POLYELECTROLYTES AIDS TO BETTER WATER QUALITY

Environmental Protection Agency
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4 June 1972

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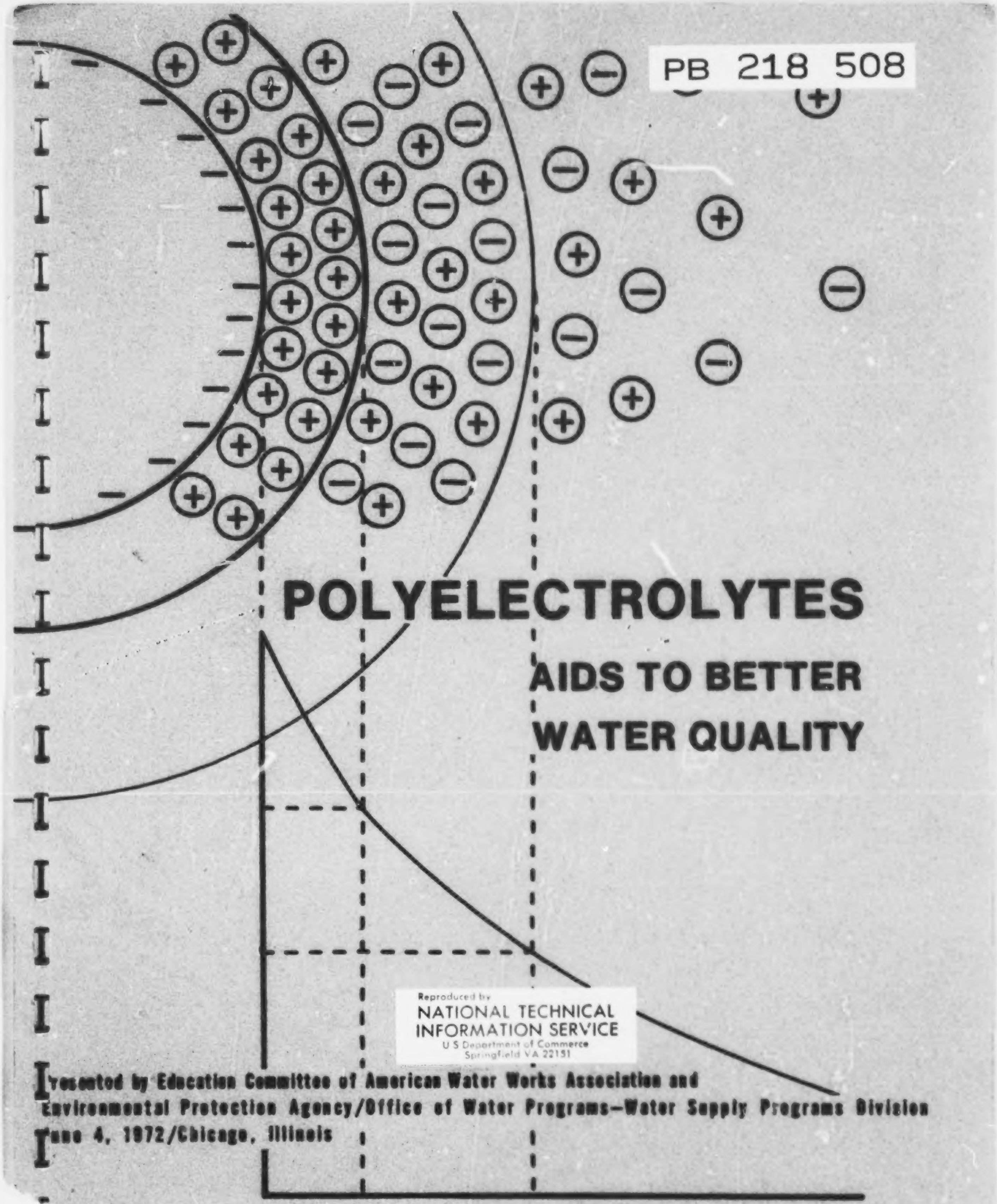

POLYELECTROLYTES

AIDS TO BETTER WATER QUALITY

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Presented by Education Committee of American Water Works Association and
Environmental Protection Agency/Office of Water Programs—Water Supply Programs Division
June 4, 1972/Chicago, Illinois

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POLYELECTROLYTES AIDS TO BETTER WATER QUALITY

Presented by

EDUCATION COMMITTEE OF AMERICAN WATER WORKS ASSOCIATION

AND

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Water Programs
Water Supply Programs Division

Chicago, Illinois

June 4, 1972

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POLYELECTROLYTES - AID TO BETTER WATER QUALITY

Chicago, Illinois

June 4, 1972

AGENDA

Moderator: E. A. Jeffrey

DAY AND TIME	SUBJECT	SPEAKER
Sunday, June 4		
9:00 - 9:10	Welcome	H. E. Hudson, Jr.
9:10 - 9:30	Hazards vs. Public Health Benefits of Polyelectrolytes	Gordon G. Robeck
9:30 - 10:30	Theory and Mechanism of Polyelectrolytes as Coagulant Aids	J. E. Singley
10:30 - 10:45	Break	
10:45 - 11:30	Purchasing, Handling, Storing and Applying Polyelectrolytes	R. A. Lo Sasso
11:30 - 12:00	Use of Polyelectrolytes as a Primary Coagulant	Timothy G. Shea
12:00 - 1:15	Lunch	
1:15 - 1:45	Use of Polyelectrolytes as Filter Aids	Robert H. Harris
1:45 - 2:15	Use of Polyelectrolytes as Aids During Backwash of Filters	W. Leslie Harris
2:15 - 2:30	Break	
2:30 - 3:00	Use of Polyelectrolytes as a Sludge Conditioner	Peter W. Doe
3:00 - 4:15	Plant Experiences	H. E. Hudson, Jr. Thomas J. Loughney Jan A. Beardsley

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Lecture	Outline Number
Hazards vs. Public Health Benefits of Polyelectrolytes	1
Theory and Mechanism of Polyelectrolytes as Coagulant Aids	2
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Use of Polyelectrolytes as a Primary Coagulant	4
Use of Polyelectrolytes as Filter Aids	5
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Use of Polyelectrolytes as a Sludge Conditioner	7

ADDENDUM

INTRODUCTION

H. E. Hudson, Jr. Chairman
AWWA Education Committee

Once again I have the pleasant duty to welcome you to this one-day seminar held prior to the American Water Works Annual Conference of 1972. As before, we have enjoyed splendid cooperation from the Water Supply Programs Division, Office of Water Programs, of EPA. In particular we are indebted to Dr. Ed Jeffrey and Gordon Robeck of that agency for the development of the program and the preparation of the course manual.

The courses planned by AWWA range from one-day units such as the three seminars that are going on simultaneously today, to one-week institutes. They include courses designed to keep water utility personnel up to date in many fields, including safety, cross-connection control, emergency planning, improving treatment plant operations, chlorination, labor relations, management seminars, and the progressive AWWA Management Institute, among others. And more such AWWA training programs are being developed. AWWA further publishes texts for use in training, such as the new basic water utility operator's manual, manuals on emergency planning, safety, management, chlorination, etc..

The bulk of this education activity carried on or sponsored by AWWA has developed in the period since the preparation of the Aims and Objective committee in 1960, and to a large extent through the work of the Association's Director of Education, Walter Peters. While we may be proud of what has been accomplished, we must also realistically be aware that training is still reaching only a small fraction of water utility personnel; and greatly-intensified efforts and financing are going to be needed to produce a training activity that is commensurate with the importance of the water utility industry. Our big problem is financing these activities, and we are still a long way from the solution to that problem. Perhaps if all of us think hard enough about this, we may come up with some solution to this problem.

Meanwhile, on behalf of the Association, I want to express my thanks particularly to Dr. Jeffrey and Mr. Robeck, and to all of the speakers today, and to all of you for your participation in the present training activity.

HAZARDS VS. PUBLIC HEALTH BENEFITS OF POLYELECTROLYTES

Gordon G. Robeck*

I HISTORY OF AWWA AND FEDERAL GOVERNMENT JOINT PROGRAM FOR REVIEW OF POLYELECTROLYTE SAFETY

A In 1957 AWWA through its Secretary, Harry Jordon, asked USPHS for advice on the safety of newly introduced synthetic "coagulant aids."

B Both parties recognized the possibility of some toxicity associated with certain portions of the aids, so a review committee was formed to pass on the safety of these products, and the following press release announced the objectives, membership and procedure for conducting the committee affairs:

August 30, 1957

"Following numerous inquiries from health agencies and at the request of the Executive Secretary of the American Water Works Association, the Public Health Service has established a public advisory committee on coagulant aids. The Committee will advise the Public Health Service as to the safety of various coagulant aids proposed for use in public water supply treatment.

"Designated as the Technical Advisory Committee on Coagulant Aids for Water Treatment, the group's function is to receive information from producers and purveyors of these materials relative to their composition and toxicity, to review such information and to advise the Assistant Surgeon General, Chief Engineer, of the Public Health Service as to the safety of these coagulant aids for use in treating drinking water. Recommendations of the Committee will be utilized by the Public Health Service in carrying out its statutory responsibility in the field of public water supplies.

"At its first meeting at the Robert A. Taft Sanitary Engineering Center, Cincinnati, on August 30, the Committee established operating procedures and policies to be followed in carrying out its work. Committee members are Dr. Herbert E. Stokinger, Public Health Service, Chairman; Dr. A. P. Black, University of Florida; Dr. David W. Fassett, Eastman Kodak Company; Mr. Paul D. Haney, Black and Veatch; Dr. Robert A. Kehoe, Kettering Laboratory, and Dr. Richard L. Woodward, Public Health Service, Secretary.

"Major manufacturers of coagulant aids have been notified of the committee's formation and will be invited to submit information on their products. Further information can be obtained from the Secretary of the Committee, c/o Robert A. Taft Sanitary Engineering Center, 4676 Columbia Parkway, Cincinnati, 26, Ohio."

A copy of the order establishing the Committee is attached.

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*Director, Water Supply Research Laboratory, EPA, Cincinnati, Ohio

TECHNICAL ADVISORY COMMITTEE ON COAGULANT AIDS FOR WATER TREATMENT

Authority–To be established administratively pursuant to Sections 301 and 311 of the Public Health Service Act (P. L. 410 - 78th Congress), as amended.

Purpose–To present technical advice to the Chief, Division of Sanitary Engineering Services. Conclusions of the Committee to be made available to the American Water Works Association, members of the water works profession, State and other public authorities, and individuals having responsibilities in the field of water supply.

Structure–Consists of five members and a Secretary, appointed by the Chief, Division of Sanitary Engineering Services, for a term of three years. One of the members, designated by the Chief, Division of Sanitary Engineering Services, is to serve as Chairman. Members are to include Federal and non-Federal representation recognized as possessing expert knowledge of water works technology, water supply chemistry, and toxicology. Close consultation will be maintained with representatives of the American Water Works Association.

Function–The first function of the Committee will be to receive from producers and purveyors information concerning the composition and characteristics of new coagulant aids proposed for use in the treatment of public water supplies. The information submitted will include data relative to the proposed use of the material for water purification, methods of applicaion, recommended dosage, etc. The information will also include data relative to the toxicological chemical, and physical properties of such substances. The Committee through its Secretary will give assurance of the confidentiality of such information submitted to it as may be requested by the producer or purveyor.

The second function of the Committee will be to review and evaluate the information received by it with respect to specific materials proposed for use in the treatment of public water supplies, and to determine whether, in its opinion, the material in question may be safely used for the treatment of public water supplies without adverse physiological effect upon the individuals consuming such water. When the information provided to the Committee by the producer or purveyor of a new material is not sufficient to enable the Committee to reach a firm conclusion, the Committee through its Secretary shall so inform the producer or purveyor of the material.

The third function of the Committee will be to report to the Chief, Division of Sanitary Engineering Services, the conclusions reached following evaluation of the information relating to each material, advising him either that (a) the material is safe for the proposed use, or (b) unsafe for the proposed use.

Meetings–The Committee will meet at the call of the Chief, Division of Sanitary Engineering Services, or of the Committee Chairman as may be necessary to carry out its function.

C The first approved list with 9 products from 5 manufacturers was released February 1958 and then quarterly announcements with additional suppliers have been made generally, including the Journal of AWWA. The current list is given for your future reference.

APRIL 1972

REPORT ON COAGULANT AIDS FOR WATER TREATMENT

On the basis of information submitted by the manufacturers and/or distributors, the Environmental Protection Agency has concluded that the following additional products may be used in water treatment without adverse physiological effects on those using the water, when applied in the concentration recommended by the manufacturers and/or distributors and provided the products continue to meet the quality specifications furnished.

MANUFACTURER AND/OR DISTRIBUTOR	PRODUCT	MAXIMUM CONCENTRATION RECOMMENDED - mg/ℓ
Allied Colloids, Inc. One Robinson Lane Ridgewood, N. J. 07450	Percol LT-20	1
	Percol LT-22	1
	Percol LT-26	1
	Percol LT-29	1
American Cyanamid Co. Wayne, New Jersey 07470	MAGNIFLOC 573-C	10
	MAGNIFLOC 575-C	10
	MAGNIFLOC 577-C	10
	MAGNIFLOC 579-C	10
Betz Laboratories, Inc. Somerton Road Trevose, Pa. 19047	Betz Polymer 1150P	1
	Betz Polymer 1250P	1
	Betz Polymer 1160P	1
	Betz Polymer 1260P	1
Commercial Chemical Products, Inc. 11 Paterson Avenue Midland Park, N.J. 07432	Speedifloc #2	5
Drew Chemical Corp. 701 Jefferson Road Parsippany, N.J. 07054	AMERFLOC 265	1
	AMERFLOC 275	1
	AMERFLOC 307	1
	DREWFLOC 4	5

MANUFACTURER AND/OR DISTRIBUTOR	PRODUCT	MAXIMUM CONCENTRATION RECOMMENDED - mg/l
E. I. Du Pont de Nemours and Company Eastern Laboratory Gibbstown, N. J. 08027	Carboxymethyl-cellulose	1
Henry W. Fink and Co. 6900 Silverton Avenue Cincinnati, Ohio 45236	No. 116 Kleer Floc	1
	No. 119 Kleer Floc	5
James Varley and Sons, Inc. 1200 Switzer Avenue St. Louis, Missouri 63147	VARCO-FLOC	150

The Environmental Protection Agency emphasizes that its findings bear only on the health aspects of the use of these products in drinking water treatment and do not constitute endorsement or indicate effectiveness for the proposed use.

A fish kill was reported to have been caused by a coagulant aid that was used to treat a water impoundment for removal of turbidity. Some of the products listed may kill fish at or below maximum recommended concentration. The review of the suitability of these products is confined to their use in drinking water treatment. Information on fish toxicity, biointensification and biodegradability will be necessary for other types of application, and users should obtain such information from the manufacturers.

The total list of products reviewed in the past and found to be suitable for use in water treatment, and that the manufacturer and/or distributor want to have listed, follows.

MANUFACTURER AND/OR DISTRIBUTOR	PRODUCT	MAXIMUM CONCENTRATION RECOMMENDED - mg/l
Allied Colloids, Inc. One Robinson Lane Ridgewood, N. J. 07450	Percol LT-20	1
	Percol LT-22	1
	Percol LT-24	5
	Percol LT-25	5
	Percol LT-26	1
	Percol LT-29	1
Allstate Chemical Co. Box 3040 Euclid, Ohio 44117	ALLSTATE NO. 2	3.0
	ALLSTATE NO. 6	1
Allyn Chemical Co. 2224 Fairhill Road Cleveland, Ohio 44106	Claron	1.5
	Claron #207	2

MANUFACTURER AND/OR DISTRIBUTOR	PRODUCT	MAXIMUM CONCENTRATION RECOMMENDED - mg/l
American Cyanamid Co. Berdan Avenue Wayne, N.J. 07470	Superfloc 127	1
	Magnifloc 521-C	10
	Magnifloc 570-C	10
	Magnifloc 571-C	10
	Magnifloc 573-C	10
	Magnifloc 575-C	10
	Magnifloc 577-C	10
	Magnifloc 579-C	10
	Magnifloc 845-A	1
	Magnifloc 846-A	1
	Magnifloc 847-A	1
	Magnifloc 860-A	1
	Magnifloc 971-N	1
	Magnifloc 972-N	1
	Magnifloc 985-N	1
	Magnifloc 990-N	1
Atlas Chemical Industries, Inc. Wilmington, Del. 19899	SORBO	20
Berdell Industries 28-01 Thomson Avenue Long Island City, N.Y. 11101	Berdell N-489 Flocculant	1
	Berdell N-821 Flocculant	1
	Berdell N-902 Flocculant	1
Betz Laboratories, Inc. Somerton Road Trevose, Pa. 19047	Betz Polymer 1100P	1
	Betz Polymer 1110P	1
	Betz Polymer 1120P	1
	Betz Polymer 1130P	1
	Betz Polymer 1150P	1
	Betz Polymer 1160P	1
	Betz Polymer 1200P	1
	Betz Polymer 1205P	1
	Betz Polymer 1210P	1
	Betz Polymer 1220P	1
	Betz Polymer 1230P	1
	Betz Polymer 1250P	1
	Betz Polymer 1260P	1
	Poly-Floc 4D	25
Bond Chemicals, Inc. 1500 Brookpark Road Cleveland, Ohio 44109	Bondfloc No. 1-101	5
The Burtonite Company Nutley, N.J. 07110	Burtonite #78	5

MANUFACTURER AND/OR DISTRIBUTOR	PRODUCT	MAXIMUM CONCENTRATION RECOMMENDED - mg/ℓ
Calgon Corporation P. O. Box 1346 Pittsburgh, Pennsylvania 15222	Coagulant Aid #2	1
	Coagulant Aid #18	15
	Coagulant Aid #233	1
	Coagulant Aid #243	1
	Coagulant Aid #253	1
	Coagulant Aid #961	5
	Cat-Floc	7
	Cat-Floc B	10
Commercial Chemical Products, Inc. 11 Paterson Avenue Midland Park, N.J. 07432	Coagulant Aid Speedifloc #1	10
	Speedifloc #2	5
Dearborn Chemical Div. W. R. Grace and Co. Merchandise Mart Plaza Chicago, Illinois 60654	Aquafloc 408 (liquid)	50
	Aquafloc 409	1
	Aquafloc 411	2
	Aquafloc 422	1
Dow Chemical U.S.A. Barstow Building 2020 Dow Center Midland, Mich. 48640	Dowell M-143	5
	PEI-1090	5
	Purifloc A-22	1
	Purifloc A-23 (PWG)	1
	Purifloc C-31	5
	Purifloc N-17	1
	Separan AP-30	1
	Separan AP-273 Premium	1
	Separan NP-10 Potable Water Grade	1
	SA-1704.2	1
	*XD 7817	1
Drew Chemical Corp. 701 Jefferson Road Parsippany, N.J. 07054	Drewfloc 1	1:8 Alum: 0.5:10 Lime**
	Drewfloc No. 3	3
	Drewfloc No. 21	5
	Drewfloc 922	10
	AMERFLOC 265	1
	AMERFLOC 275	1
	AMERFLOC 307	1
	Drewfloc 4	5
DuBois Chemicals Div. of W. R. Grace and Co. 3630 E. Kemper Road Sharonville, Ohio 45241	FLOCCULITE 550	2

*Name Change

**One part of Drewfloc to 8 parts of alum when used simply as an aid in alum coagulation, and 0.5 mg/ℓ of Drewfloc to 10 mg/ℓ of lime when used in connection with lime softening.

MANUFACTURER AND/OR DISTRIBUTOR	PRODUCT	MAXIMUM CONCENTRATION RECOMMENDED - mg/l
E. I. DuPont de Nemours and Company Eastern Laboratory Gibbstown, N. J. 08027	Carboxymethylcellulose	1
Henry W. Fink and Co. 6900 Silverton Avenue Cincinnati, Ohio 45236	No. 102	1
	No. 109 Kleer-Floc	1
	No. 116 Kleer-Floc	5
	No. 119 Kleer-Floc	1
	No. 730 Kleer-Floc	1
	No. 735 Kleer-Floc	1
Gamlen Sybron Corp. 321 Victory Avenue S. San Francisco Calif. 94080	Gamlose W	5
	Gamlen Wisprofloc 20	5
	Gamafloc NI-702	4
Garrett-Callahan 111 Rollins Road Millbrae, California 94031	Coagulant Aid 72A	50
	Coagulant Aid 74B	30
	Coagulant Aid 76	40
	Coagulant Aid 76A	50
	Coagulant Aid 78B	50
	Formula 70A	50
	Formula 73	50
	Formula 74E	20
General Mills Chemicals 4620 W. 77th Street Minneapolis, Minnesota 55435	SuperCol Guar Gum	10
	Guartec F	10
	Guartec SJ	10
Hercules, Inc. 910 Market Street Wilmington, Del. 19899	Carboxymethylcellulose	1
	Hercofloc 818 (Potable Water Grade)	1
	Hercofloc 821 (Potable Water Grade)	1
Frank Herzl Corp. 299 Madison Avenue New York, N.Y. 10017	Perfectamyl A5114/2	10
Illinois Water Treatment Co. 840 Cedar Street Rockford, Illinois 61102	Illco IFA 313	10
Kelco Company 8225 Aero Drive San Diego, California 92123	Kelgin W	2
	Kelcosol	2

MANUFACTURER AND/OR DISTRIBUTOR	PRODUCT	MAXIMUM CONCENTRATION RECOMMENDED - mg/l
Key Chemicals 4346 Tacony Philadelphia, Pa. 19124	Key-Floc-W	25
Metalene Chemical Co. Bedford, Ohio 44014	Metalene Coagulant P-6	5
The Mogul Corporation 20600 Chagrin Blvd. Cleveland, Ohio 44122	Ecco Suspension Catalyzer 146	3.5
	MOGUL CO-980	2
	MOGUL CO-982	1.5
	MOGUL CO-983	1
	MOGUL CO-985	3.5
	MOGUL CO-986	5
Nalco Chemical Co. 6216 W. 66th Place Chicago, Ill. 60638	Nalcolyte 110A	5
	Nalcolyte 607	7
	Nalcolyte 671	1
	Nalcolyte 7870	1
	Nalcolyte 8170	1
	Nalcolyte 8173	1
	Nalcolyte 8175	1
Narvon Mining & Chem. Co. Affiliate of Irl Daffin Assoc. Keller Ave. and Fruitville Pike Lancaster, Pa. 17604	Sink-Floc Z3 and AZ-3	10
	Sink-Floc Z4 and AZ-4	10
	Sink-Floc Z5 and AZ-5	10
	Zeta-Floc C	20
	Zeta-Floc K	20
	Zeta-Floc O	20
	Zeta-Floc WA	20
National Starch and Chem. Corp. 1700 W. Front Street Plainfield, N.J. 07063	Floc-Aid 1038	5
	Floc-Aid 1063	5
O'Brien Ind., Inc. 95 Dorsa Avenue Livingston, N. J. 07039	O'B Floc	10
Oxford Chemical Div. Consolidated Foods Corp. P. O. Box 80202 Atlanta, Georgia 30341	OXFORD-HYDRO-FLOC	10

MANUFACTURER AND/OR DISTRIBUTOR	PRODUCT	MAXIMUM CONCENTRATION RECOMMENDED - mg/l
W. A. Scholten's Chemische Fabrieken M. V. Foxhol, Postbus 1 The Netherlands	Wisprofloc P	5
Standard Brands Chem. Ind., Inc. Div. of Std. Brands P. O. Drawer K Dover, Del. 19901	TYCHEM 8035	1
A. E. Staley Mfg. Co. P. O. Box 151 Decatur, Ill. 62525	HAMACO 196	5
Stein, Hall and Co., Inc. 605 Third Avenue New York, N. Y. 10016	Hallmark 81	1
	Hallmark 82	1
	Jaguar	0.5
	MRL-14	1
	MRL-22	1
	Polyhall M-295 P. W.	1
James Varley and Sons, Inc. 1200 Switzer Avenue St. Louis, Missouri 63147	VARCO-FLOC	150
W. E. Zimmie, Inc. 810 Sharon Drive Westlake, Ohio 44145	Zimmite ZM-100	1
	Zimmite ZC-301	130
	Zimmite ZT-600	1
	Zimmite ZT-601	1
	Zimmite ZT-603	

D The review process has been modified somewhat in the mid-sixties, by having mainly governmental toxicological evaluation of company confidential test data. The protocol for obtaining approval follows.

GUIDELINES FOR THE INFORMATION NEEDED FOR EVALUATION OF ACCEPTABILITY OF NEW PRODUCTS AND FORMULATIONS INTENDED FOR USE AS

COAGULANT AIDS FOR WATER TREATMENT

INTRODUCTION

One of the primary concerns in the use of water coagulant aids is that they contribute no hazard to man's health; consequently, there must exist assurance that the benefits of the new technologies and new products are attained with minimal risk to man's health and well-being.

The Committee on Coagulant Aids for Treatment of Drinking Water serves as the mechanism for the review and acceptance or rejection of chemicals for treatment by coagulation of potable water on the basis of their safety for such use. The membership of the Committee consists of professionals in Toxiocology, Chemistry, Water Treatment, and related fields.

Certain basic information is needed in order for the Committee to evaluate the acceptability of each coagulant aid for which approval is requested. These requirements are covered in Sections I and II. In no case will the Committee consider products without complete information on their composition. If the material is to be treated as confidential, the petitioner should indicate this preference, and his wishes will be respected.

Because coagulant aids are applied to water consumed under varied environmental conditions and for prolonged periods by the public, which includes individuals of all ages and susceptibilities, stringent safeguards for health protection must apply. The chemicals under consideration are not essential to the production of potable water but rather are useful and economic additives in water treatment. For these reasons, the Committee requires that the safety of low-exposure long-term use as well as higher-exposure shorter-term use of the proposed material be demonstrated by evidence that leave no reasonable basis for doubt.

The minimum for acceptable toxicologic data concerning all new products is a definitive study of the effects sustained by experimental animals such that the results may be projected to man. This objective can rarely be achieved in less than one year of investigation. Section III lists suggested toxicologic studies. The minimum number of levels of concentrations in water (or other suitable media) to be administered to animals over a prolonged period is three: The concentration recommended for use, 10 times that concentration, and 100 times the recommended concentration.

If a material is known to be without harmful physiological effects on the basis of (a) controlled epidemiologic and toxicologic studies, (b) previously demonstrated acceptability, or (c) existence as a normal constituent of foodstuffs, some of the studies called for under Section III may be unnecessary. However, only minimum requirements are given, and it is not intended that they be construed as limiting the volume of data that should be developed in evidence of safety. Rather, it is more important that the investigations be tailored to fit to toxicological needs of the compound under test. For example, if it appears that the substances produces changes in the cellular elements of the blood. experiments should be so designed as to explore in some depth the nature of these changes by more sensitive and more specific techniques.

Toxicological investigations should be designed to produce information pertinent to the question of long-term safety of use of the product as a water treatment chemical. It should be appreciated also that the advice of qualified investigators should be sought in designing and performing the toxicologic studies.

Three (3) copies of all petitions should be directed to:

Secretary, Committee on Coagulant Aids
for Treatment of Drinking Water
Water Supply Programs Division
Environmental Protection Agency
4676 Columbia Parkway
Cincinnati, Ohio 45268

The petitioner will be notified directly as to the decision of the Committee within 30 to 90 days after submission of all data.

I CHEMICAL PROPERTIES

A Composition

1 Physical and chemical composition (names, structures, and quantities) of constituents of the product.

2 All pertinent physical and chemical properties and specifications for ingredients of the commercial product, including lipid solubility and molecular weight distribution.

3 If the substance is a polymer: a detailed description of methods used to characterize the products and assure its uniformity, including monomer content (%).

4 Analytical methods for determination of residues of both polymer and monomer in water, including information on sensitivity, accuracy, and precision.

B Impurities, Nature and Amounts, Including Heavy Metals.

C Data Demonstrating Uniformity of Product and Description of Quality Control Processes.

D Stability in Storage.

E Reaction in water, including possible changes at elevated temperatures such as may be encountered in domestic water heaters, and at pH values from 5.0 to 11.0, and characterization of degradation production.

F Reaction with other water treatment chemicals, such as, chlorine, and with known contaminants of drinking water such as heavy metals and characterization of reaction products.

G Data on residues of monomer and polymer remaining in water after treatment under conditions of use not only when additional water treatment is used, but also when no other water treatment is used.

H All Trade and Proprietary Names.

I Uses in Other Edible Materials and Amounts Proposed or Approved by Other Agencies Should be Stated.

J Label of Product as Sold.

II CONDITIONS OF USE

A Recommended Levels of Dosage.

B Method of Application Including Industrial Experience Relating to Hazards and Safe Practices in Handling.

C Dose-response data relating concentration of the product in water with the ability to coagulate suspended and dissolved material in waters having different chemical characteristics.

III EVIDENCE OF TOXICITY

The following types of experiments are commonly undertaken to develop information necessary to judge the acceptability of the product from the standpoint of human health. It is not intended that all procedures given below are required in each instance or that additional studies may not be required in some cases. Emphasis should be placed on studies that demonstrate high sensitivity, high specificity and clincical relevance. Decisions on such questions should be made by competent investigators. Some procedural detail is given to provide some degree of uniformity in information submitted to the Committee on various products to aid its work of evaluation.

If the products is a polymer, these studies should be conducted on the monomer as well as the polymer, if feasible. These investigations should be designed to establish differences in susceptibility, if any, according to sex, species (rodent and non-rodent), age, and disease status. Since the goal is to project the results to biological responses in the human population, efforts must be made to include a significant number of animals in each group in order to have some basis to judge the frequency of response. If the product is administered with food - rather than in drinking water or by gavage - it is essential to establish that, (1) the product is stable and does not undergo chemical change and, (2) the effect level obtained under these conditions does not differ significantly from that recorded with water as the vehicle.

The information submitted should be presented in the form of data that has been subjected to appropriate statistical treatment (for example: means, ranges, standard deviations, standard errors, confidence limits, significance tests, etc.). The use of tabular and graphic forms is encouraged as means of organization and clarification.

If pertinent toxicologic and epidemiologic data have been previously reported in the scientific literature, the appropriate citations may be submitted in lieu of duplicating those studies.

A Required Studies

1 Acute (single dose) toxicity

a Purposes:

1) To establish the LD 50 by oral and other routes in animals to permit relative toxicity ratings with known substances.

2) To characterize the slope of the dosage-response curve to permit more specific estimation of safe doses.

3) To note type, time of onset, severity, and duration of toxic signs and symptoms; to determine cause of death and organ damage.

b As indicated from conditions of use, the acute toxicity of the products should be determined by one or all of the routes of administration listed below.

1) Oral LD 50. Use of published (standard) methods of procedure are suggested (J. T. Litchfield, Jr., and F. W. Wilcoxon, "A Simplified Method of Evaluating Dose-Effect Experiments," J. Pharmacol. Exptl. Therap. 96:99, 1949). In the case of mixtures of substances, the acute toxicity of the entire mixture should be determined, as well as the major contributor(s) to the toxicity.

Observation time: 2 weeks.

Animals: Mice, rats, and guinea pigs; 10 animals per dose

2) Cutaneous toxicity - determination of:

a) Degree of absorption through the skin and extent of systemic effects.

b) Primary irritant effect.

3) Sensitizing properties. The standard method of Draize et al. (J. Pharmacol. Exptl. Therap. 82:377, 1944), is acceptable. The results of human experience are preferable and should be submitted, if available. Serious consideration should be given to clinical trials.

Animals: Guinea pigs and rabbits; 5 animals per dose.

c Ocular toxicity. Determination of irritation and injury (according to method of J. H. Draize "Dermal Toxicity" in Appraisal of the Safety of Chemicals in Foods, Drugs, and Cosmetics, Association of Food and Drug Officials of the U.S., Topeka, Kansas, 1965.)

d Potentiation Studies. Enhancement of sum of the individual effects caused by the administration of 2 of more chemicals to the same organism. Combination of product with environmental analogs, with heavy metals commonly found in water and with other water treatment chemicals.

2 Metabolism studies

Purpose: To generate definitive information on the degree of absorption, extent of distribution, storage, tissue localization, metabolism, half-life in the organism, routes of excretion, and nature of excretory products. Such investigations, as determination of the rate of excretion following the administration of single or repeated doses at levels selected to be non-injurious to either kidney or gastro-intestinal tract, may provide helpful information in deciding potential risks from long continued xposure.

The manner and rate of absorption of an ingested substance can be highly informative, and at times completely definitive. If, for example, it can be shown by radio-tracer, or other suitably sensitive technique, that the ingested substance under test is not absorbed, this fact in general will eliminate the need to carry out further tests other than those to determine, (a) whether the substance is an irritant to the gastro-intestinal tract or, (b) whether it may prevent absorption of essential micro-nutrients.

The design of the experiments should incorporate single and multiple dosage schedules in order to assess possible storage and cumulative effects. At least 2 animal species should be used in order to detect inter-species differences. All vital organs of the experimental animals should be assayed for residues of the test material at varying times after cessation of exposure.

B Recommended Supplemental Studies

If reliable information derived from human experience in the production, handling, and use of the material or from the administration of the coagulant aid to man is available, such information should usually take precedence over comparable data from laboratory animals. However, if such information is lacking and depending upon the type of responses obtained in the Required Studies (A.1. and A.2.), careful consideration should be given to conducting the following studies in order to obtain further information about the toxicity and possible human health effects of the coagulant aid. In order to obtain pertinent data, these studies should be tailored to the in-depth investigation of the toxic responses, as well as to the elucidation of deleterious effects resulting from chronic exposure.

1 Chronic toxicity - oral

a Purpose: Chronic oral toxicity tests are designed to provide data adequate to evaluate the safety of substances that may be ingested by man. When metabolic pathways are not known and/or unproductive of simple and safe explanations and where subacute toxicity tests have produced only minor effects, chronic toxicity tests should be carried out on the proposed chemicals. Chronic tests in contrast to subacute studies should determine with relative certainty that we are not encountering a case where the effect of exposure to a small amount of a compound for a long time differs markedly from an exposure to a large amount of the chemical for a short time. The chronic experimental data generated should be sufficient to establish a "no effect" dosage with confidence. This "no effect" level can then be used to establish the definite margin of safety.

b Animals:

1) Rats, weanlings, 50 (25 of each sex) per level with an equal number of controls. A larger number of rats per group will aid in the interpretation of results and therefore, reduce the possible risks of approving the use of a toxic substance or of missing a safe compound. If animals are to be sacrificed prior to the end of the study, the number of animals should be increased accordingly.

2) Dogs, under 1 year of age, 8 (4 of each sex) per level with an equal number of controls. Since there should be a minimum of 4 dogs remaining in each group at the termination of the experiment, the exact number used at the beginning depends upon the desirability of sacrificing animals during the experimental period and the accepted risk of losing animals from natural causes.

c Duration: One to two years.

d Levels of test material: Minimum of 3 test levels and a control.

1) One level at 10 times the concentration intended for use, or a "no effect" level, whichever represents the higher concentration.

2) One level at 100 times the concentration intended for use; or ten times the "no effect" level, whichever represents the higher concentration.

3) A level designed to produce mild adverse effects during the course of the experiment.

4) Control, no product added, vehicle only.

e Criteria for toxicity:

1) Changes in body weight, appearance, growth, food consumption, and ability to reproduce.

2) Hematologic and biochemical parameters.

3) Gross- and histo-pathologic changes of organs of fatally poisoned animals and of those sacrificed for examination.

4) Alteration of activity of specific enzymes (e.g., cholinesterase, hepatic nicrosomal oxidases, etc.), if applicable.

5) Other criteria as indicated.

2 Carcinogenicity studies

a Purpose: To determine if the coagulant aid is carcinogenic when ingested.

b Animals: Mice or rats. Ordinarily young animals are used; however, animals 10 to 12 months of age may be used.

c Duration: 12 months

d Levels: (Same as for B.1.d.).

3 Mutagenicity studies

a Purpose: To determine whether the material produces genetic mutations deleterious to the basic functions of the organism.

b Methods: A number of techniques exist to test mutagenic potential. These include the Dominant Lethal Test, Cytogenetic Studies in Cultured Mammalian Cell Lines, Cytogenetic Evaluation from Bone-Marrow Preparations of Treated Animals, Host-Mediated Studies, and Induction of Forward-Reverse Mutations in Cultures Mammalian Cell Lines. There is no preference as to the use of any of these or other tests. However, it should be noted that some of the tests can be readily incorporated into the design of chronic toxicity studies.

c Levels: (Same as for B.1.d.)

4 Teratogenicity studies

a Purpose: To demonstrate any effects upon fertility, ability to reproduce, size of litters, litter survival, etc., and to determine teratogenic and other fatal toxic effects.

b Animals:

1) Mice or rats.

2) Rabbits.

c Duration: Through the F2 generation.

IV CHANGE OF TRADE NAME OR PRODUCT DESIGNATION ONLY

A Repackaging of One Previously Approved Product, the Following are Required:

1 Written testimony from the manufacturer and distributor to the effect that the product is the same in composition and quality as that previously approved, that the original manufacturing processes have not been markedly altered, and that the repackaging process does not adulterate the product.

2 Recommended of dosage under new trade name.

3 Label of the product as sold.

B Repackaging of Combination of Two or More Previously Approved Products, the Following are Required:

1 Written testimony from the manufacturer(s) and distributor to the effect that the products are the same in composition and quality as those previously approved, that the original manufacturing processes have not been markedly altered, and that the repackaging process does not adulterate the product.

2 The data from at least three batches of the new combination to demonstrate uniformity of the product.

3 Recommended levels of dosage of combination under new trade name.

4 Label of product as sold.

5 Acute potentiation studies combining both products (see Section III.A.1.b.[4]) by the intraperitoneal and oral routes.

End of Section on Coagulant Aids for Water Treatment.

Hazard vs. Public Health Benefits of Polyelectrolytes

Cont'd from page 1.

E Recently, spot checks also have been made of products to determine the monomer content of acrylamide.

II Limited results with pilot-scale operations indicate a greater assurance of particle and thus viral removal under certain circumstances when a polyelectrolyte is used either as a coagulant or filter aid. Published data (Oct. 1962, P. 1275 and Feb. 1964, p. 198, Jour. AWWA.)

THEORY AND MECHANISM OF POLYELECTROLYTES AS COAGULANT AIDS

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There is a great deal of current interest in the use of polyelectrolytes as coagulants or as coagulant aids because: (1) the great current concern for the very large volumes of sludge that are produced in water works operation, (2) their efficiency, and (3) their ease of handling. The largest volume of the sludges of concern is produced as a result of coagulation with alum or ferric salts to generate a very gelatinous material that is very difficult to dewater and find a method of disposal. These problems became evident as a result of the 1969 Conference on the Disposal of the Waste from Water Treatment Plants sponsored by the AWWA Research Foundation, which emphasized two very important objectives in its report:

"Engineers should recognize that water treatment plant design must now include positive means for disposal of sludge. At the same time, engineers should consider economy as a basic consideration in the selection and design of disposal methods."

The Committee on Plant Operation Needs was even more specific when they concluded that "in summation, the principal needs are to find effective and economical means, through research, to dispose of water treatment plant wastes by direct treatment of sludge, or by eliminating undesirable chemicals, such as alum, through changes and water treatment methods. This need applies both to clarification and softening of surface and well waters."

Other applications for polyelectrolytes will be discussed during this seminar and include such uses as coagulant aids to supplement or partially replace metal ion salt coagulants, as primary coagulants ahead of high rate filtration, and as sludge conditioning agents.

Before considering the properties and uses of polyelectrolytes, it would be appropriate to consider first what we mean by a polyelectrolyte. The term was first suggested by Fuoss to define those organic polymers which can be converted to long chain molecules having ionized sites along their length. By the term polymer, we mean chain of sub-units that have been reacted to form a larger molecule. Some polymers contain only one type of sub-unit and these are referred to as homopolymers. Others contain different sub-units, and these are referred to as co-polymers. The sub-units themselves are referred to as monomers. The total number of monomers in the polymer chain can be varied, as well as the types of monomers, so that a wide variety of polymers can be produced. These polymer chains may be linear or may contain much branching of chains and may have a variety of ionizable groups at various locations on the chain. If the polymer contains ionizable groups along the chain it is referred to as a polyelectrolyte; "poly," of course, meaning many. Those polymers that retain a negative charge on the chain after ionization are referred to as anionic polyelectrolytes; those that retain a positive charge on the chain are referred to as cationic; and those that contain both positive and negative charges are referred to as ampholytic polyelectrolytes. There are, of course, polymers which contain no charged sites, or at least no ionizable groups, on the chain and these are referred to as non-electrolytes or non-ionic polymers. Examples of the structures of representative examples of each of these classes of polymers are shown in Figure 1. The effectiveness of any of these polymers in coagulation and flocculation is obviously a function of their tendency to react with the substances to be coagulated. The properties of these polymers are influenced by the chemical structure as well as the environment in which they are found. It can be seen from Figure 1 that many of the ionizable groups may be strongly affected by changes in pH. Other groups could be affected by specific ionic interactions. The geometry of the polymer molecule in solution is a function of the same parameters. In cases where like charges are neutralized by the presence of indifferent electrolytes the polymer chains are more likely to be randomly coiled because of the reduced electrostatic repulsions. In solutions of very low ionic strength, the polymer chains may be extended and almost linear in structure. These factors, of course, influence the behavior of such molecules.

Before discussing the use of polyelectrolytes to coagulant colloids, we should probably summarize the properties of colloids themselves. It is well known that most natural colloids are negatively charged and it is this charge that is largely responsible for the stability of such colloids. The particles themselves are so small that they are not affected appreciably by gravity and do not settle rapidly enough in water for their removal to be accomplished in this manner. It can be estimated that particles in the colloidal size range take up to 63 years to settle a distance of one foot. This makes it obvious that the very small particles must be agglomerated into particles large enough to settle much more rapidly. Colloids themselves may contain ionizable groups on the surface or near enough the surface for the counter ions to difuse into the bulk of the solution, thereby leaving a residual charge on the particle surface. Since the majority of such ionizable groups in nature are negatively charged, colloids themselves are negatively charged. Colloidal particles could be destabilized by driving them together with sufficient energy to overcome the electrostatic repulsive forces and getting them close enough together so that van der Waal's forces of attraction could bind them. It has been shown that the energies required cannot be accomplished in an economical manner. This means that some other mechanism must be used in order to agglomerate the particles. There are two basic theories of the effect of coagulants on colloidal particles. The first of these, the chemical theory, emphasizes specific chemical interactions whereas the second, the physical theory, emphasizes physical interactions. The chemical theory views the colloids as particles of definite chemical structural units that react specifically with the coagulant. Then the coagulation results from the precipitation of insoluble complexes. The physical theory is based on the reduction of the effective particle charge, thereby allowing the particles to approach more closely. This theory requires recognition of the so-called double-layer structure of colloidal particles that is credited to Stern and Guoy. Since a colloidal system cannot have a net electrical charge, the charge on the colloid particles themselves must be balanced by an equal number of oppositely charge ions in solution. At the interface between the solution and the colloidal particle an electrical potential exists. Counter ions are attracted to the interface proportionally to the magnitude of the charge. The distribution of counter ions in solution is a function of the number of counter ions that are available. A picture of the double-layer model for colloidal particles is shown in Figure 2. The charge on these particles cannot be measured directly since part of the double-layer of counter ions accompanies the particle when it moves through solution, whether induced thermally, physically, or by imposition of a potential difference across the system. The charge at the slipping plane is referred to as the zeta potential. This is the potential that can be measured, rather than the potential at the surface of the colloidal particle, the so-called Nernst potential. The distribution of this potential can be influenced by the concentration of counter ions in solution. This is shown in Figure 3 for a high concentration of electrolytes in solution. This figure can be compared with Figure 2 to see the effect of higher concentrations of counter ions. Polyvalent counter ions are, of course, more effective than monovalent counter ions because of their higher charge densities and consequently greater ability to be accommodated more closely to the charged particle surface. This effect is shown in Figure 4. The well-known Schulze-Hardy rule relates the relative coagulating powers of charged ions. A divalently charged ion is approximately 50 to 70 times as effective in neutralizing the charge on the colloidal particle as is a monovalent ion and a trivalent ion is six to seven-hundred times as effective.

In order to understand the effect of polyelectrolytes on colloids, it is necessary to combine the the physical and chemical theories and produce a more general theory of particle destabilization. It has been shown that simple charge neutralization is in itself relatively ineffective in the coagulation of naturally occurring colloids in water. Several obvious anomalies occur when attempts are made to invoke the charge neutralization theory or colloidal destabilization with both organic and inorganic polymers. For example, it has been found that iron and aluminum salts are effective in destabilizing colloids at zeta potentials near, but seldom at exactly, zero zeta potential. In addition, there are many examples in the literature of destabilization of negatively charged colloids with anionic polyelectrolytes. Such results obviously cannot be explained by a simple electrostatic model.

Currently, our best explanation of the mechanism by which polyelectrolytes destabilize colloids is based on adsorption of the polyelectrolytes on the surface of the colloidal particles followed by either reduction of the charge or bridging between colloidal particles by the polyelectrolyte itself. These two possible mechanisms of particle aggregation are not easy to differentiate. There are certainly both chemical and physical factors involved. The attraction of the polymer particles to the colloidal surface may be predominantly a chemical property or it may be a simple physical property. Organic polyelectrolytes, by their very nature, tend to be relatively insoluble in water. This, of course, due to their long organic chain which is essentially hydrophobic. They tend to congregate at any interface of the aqueous solution with either solid particles, the container, or the atmosphere. This rejection of the organic portion of the polyelectrolyte by the solution is not complete because of the ionizable sites or the partially charged sites on the polymer itself. This part of the molecule is attracted to the aqueous phase. No specific interaction is required in such cases; it is only necessary that the interface be less repulsive than then aqueous phase itself. Figure 3 shows a schematic diagram of adsorption and subsequent interaction of the polymer particles with a colloidal particle. It shows several steps in the interaction between the two. After the initial adsorption of the polymer chain may undergo several possible configurations. It may continue to rap around the particle. This, of course, occurs under conditions in which the polymer chain itself is rather compact or coiled and does not extend out into the solution. When high concentrations of polyelectrolytes are present, this may, in fact, be the result. The colloidal particles can be restabilized by high concentrations through this mechanism. If on the other hand the polyelectrolyte chain is extended, only a part of the chain is attached to the colloidal particle with the remainder extended into the bulk of the solution. This particular theory was proposed by Nenckel and Rumbach to explain the fact that more polymer could be adsorbed on a particle than a simple monolayer would allow. The extended parts of the chains may then interact with other extended chains or even with other particles. If the particle that is attached to the colloid is oppositely charged to the charge on the colloid, then charge neutralization may result. This would allow partially destabilized or partially charged neutralized colloidal particles to approach closely enough for the van der Waal's forces of attraction between colloid and colloid or colloid and polymer or polymer and polymer chains to take place. These interactions would result in particle agglomeration and would result, ultimately, in colloidal destabilization and subsequent sedimentation. There have been many important papers in the literature that have substantiated and provided useful information for the development and confirmation of these theories. A number of those are cited in the table of references at the end of this paper, rather than being cited individually.

Some of the apparently anomalous results obtained in studies of polyelectrolytes interacting with colloids can be explained in terms of the above suggested mechanisms. For example, the destabilization of negative colloids with anionic or nonionic polymers may now seem more reasonable. If the adsorption energy exceeds the repulsive energy, then the adsorption step will predominate. It was shown by Black, Birkner, and Morgan that the presence of calcium ions strongly affects the anionic polymer-colloid systems. They studied destabilization of clay particles with hydrolized polyacrylic acid polymers. They explained the effect of calcium ion on the interaction by pointing out that calcium ions would effectively reduce the electrostatic repulsive forces between clay particles by double-layer compresion and further reduce the repulsive forces between anionic polyelectrolyte and the negatively charged clay particles. Further, they would reduce the repulsive forces between the negative sites on adsorbed polymer molecules. Each of these factors would lead to increased adsorption of polymer onto the colloid particle or to destabilization of the clay particles themselves or the clay particles with adsorbed polymer. Sommerauer, Sussman, and Stumm provided additional information on this phenomenon. They pointed out that calcium ions can form specific complexes with some of the ionizable groups on the colloidal particle and on the polymer chain. In general it has been shown that long chain anionic polymers are more effective in clay coagulation than on short chain polymers with the same degree of hydrolysis. This would tend to support the idea of inter-particle bridging for this particular type of destabilization.

Cationic polyelectrolytes should be effective at lower concentrations than anionic or nonionic polyelectrolytes since they can act to neutralize particle charge as well as to provide inter-particle bridging. One consequence of this is that lower molecule weight cationic polyelectrolytes should be more effective than similar molecular weight polymers with negative or no charge. Figure 6 shows a comparison of the optimum concentrations of several coagulants for destabilization of colloidal systems. This figure is taken from that shown by O'Melia. The coagulants considered are the simple sodium, calcium and aluminum ions as compared to dodecylammonium ion and a partially hydrolyzed polyacrylamide. The dramatic difference in the optimum coagulation concentration confirms the theory that charge neutralization is not the major factor in destabilization by polyelectrolytes.

The use of polyelectrolytes in other applications such as replacement of part of a metal ion coagulant or sludge thickening may generally be an application of the bridging mechanism to bind together the very small microflocs that have been produced by some other process, but which do not produce the large enough particles to settle or to be removed readily by filtration. Adsorption of polyelectrolytes on filter media may provide a charged surface on the media that would attract and bind colloidal particles to that surface. The mechanisms that have been discussed should allow the water chemist or engineer to design effective coagulation systems, or at least to understand better the performance of specific coagulants under a given set of circumstances. Ultimately, this will lead to improved water treatment and higher quality finished water.

REFERENCES

Birkner, F. A. and Edzwald, J. K. Nonionic Polymer Flocculation of Dilute Clay Suspensions. Jour. AWWA, 61:645, December, 1969.

Birkner, F. B., and Morgan, J. J., "Polymer Flocculation Kinetics of Dilute Colloidal Suspensions," Journal, American Water Works Association, Vol. 60, 175-191 (1968).

Black, A. P., Birkner, F. B., and Morgan, J. J., "Destabilization of Dilute Clay Suspensions with Labeled Polymers," Journal, American Water Works Association, Vol. 57, 1547-1560 (1965).

Coagulant Aids for Potable-Water Treatment, Journal, American Water Works Association, Vol. 59, 212, 650 (1967).

Cohen, J. M., Rourke, G. A., and Woodward, R. L. "Natural and Synthetic Polyelectrolytes as Coagulant Aids," Journal, American Water Works Association, Vol 50, 463 (1958).

Committee Report, "State of the Art of Coagulation," Journal, AWWA, 63:99 (February 1971).

Conley, W. R., and Pitman, R. W., "Test Program for Filter Evaluation at Hanford," Journal, AWWA, 52:205 (1960).

Conley, W. R., and Pitman, R. W., "Innovations in Water Clarification," Journal, AWWA, 52:1319 (1960).

Dixon, J. K. et al., "Effect of Structure of Cationic Polymers on the Flocculation and Electrophoretic Mobility of Crystalline Silica," Journal, Colloid Sci., 23:465 (1967).

Fuoss, R. M. and Cathers, G. I., "Polyelectrolytes. I. Picrates of 4-Vinyl-Pyridine-Styrene Copolymers," J. Polymer Sci., 2:12 (1947).

Jenckel, E., and Rumbach, B., "The Adsorption of High Molecular Weight Materials from Solution," Ger. Z. Elektrochem, 55:612 (1951).

Johnson, C. E., "Polyelectrolytes as Coagulants and Coagulant Aids," Ind. Eng. Chem., 48:1080 (1956).

Kleber, J. P., "Field Use of a Cationic Polymer for Clarification," Water and Wastes Eng., 6(6):42(69).

Korla, J., Ullman, R., and Eirich, F. R., "The Adsorption of Polyvinyl Acetate," J. Phys. Chem., 62:541 (1958).

LaMer, V. K., "Filtration of Colloidal Dispersions Flocculated by Anionic and Cationic Polyelectrolytes," Faraday Society Discussion, No. 42, 248-254 (1966).

LaMer, V. K., and Healy, T. W., "Adsorption-Flocculation Reactions of Macro-molecules at the Solid-Liquid Interface," Rev. Pure and Appl. Chem., 13:112 (1963).

Mueller, K. C., and Burbank, W. C., Jr., "Effects of Polyelectrolyte Coagulant Aids on Removal of Missouri River Turbidity," Journal, AWWA, 56:333 (1964).

Michaels, A. S., "Aggregation of Suspensions by Polyelectrolytes," Industrial and Engineering Chemistry, Vol. 46, 1485-1490 (1954).

Mysels, K. J., Introduction of Colloid Chemistry, pp. 77-82, Interscience Publishers, Inc., New York, (1959).

O'Melia, C. R., "A Review of the Coagulation Process," Public Works, Vol. 100, 87-98, May (1969).

Oulman, C. S., Burns, D. E., and Baumann, E. R., "Effect on Filtration of Polyelectrolyte Coatings of Diatomite Filter Media," Journal, AWWA, 56:1233 (1964).

Peterson, C., and Kwei, T. K., "The Kinetics of Polymer Adsorption onto Solid Surfaces," J. Phys. Chem., 65:1330 (1961).

Pugh, T. and Heller, W. "Coagulation and Stabilization of Colloid Solutions with Polyelectrolytes," Journal, Poly. Sci., 47:219 (1960).

Pressman, M., "Cationic Polyelectrolytes as Prime Coagulants in Natural Water Treatment," Jour. AWWA, 59:169 (1967).

Riddick, T. M., "Zeta Potential and Polymers," Journal, AWWA, 58:719 (1966).

Robeck, G. G., Dostal, K. A., and Woodward, R. L., "Studies of Modifications in Water Filtration," Journal, AWWA, 56:198 (1964).

Smoluchowski, M., "Versuch einer mathematischen Theorie der Koagulationskinetik kolloider Losungen," Zeitschrift fur physicalische Chemie, Vol. 92, 129-168 (1917).

Sommerauer, A., Sussman, D. L., and Stumm., W., "The Role of Complex Formation in the Flocculation of Negatively Charged Sols with Anionic Polyelectrolytes," Kolloid-Zeitschrift and Zeitschrift fur Polymere, Vol. 225, 147-154, (1968).

Stumm, W., and Morgan, J. J., "Chemical Aspects of Coagulation," *Journal, AWWA*, Vol. 54, 971-994 (1962).

Stumm, W., and O'Melia, C. R., "Stoichiometry of Coagulation," *Journal, AWWA*, Vol. 60, 514-539, (May, 1968).

Verwey, E. J. W., and Overbeek, J. T. G., "Theory of the Stability of Lyophobic Colloids," Elsevier, New York (1948).

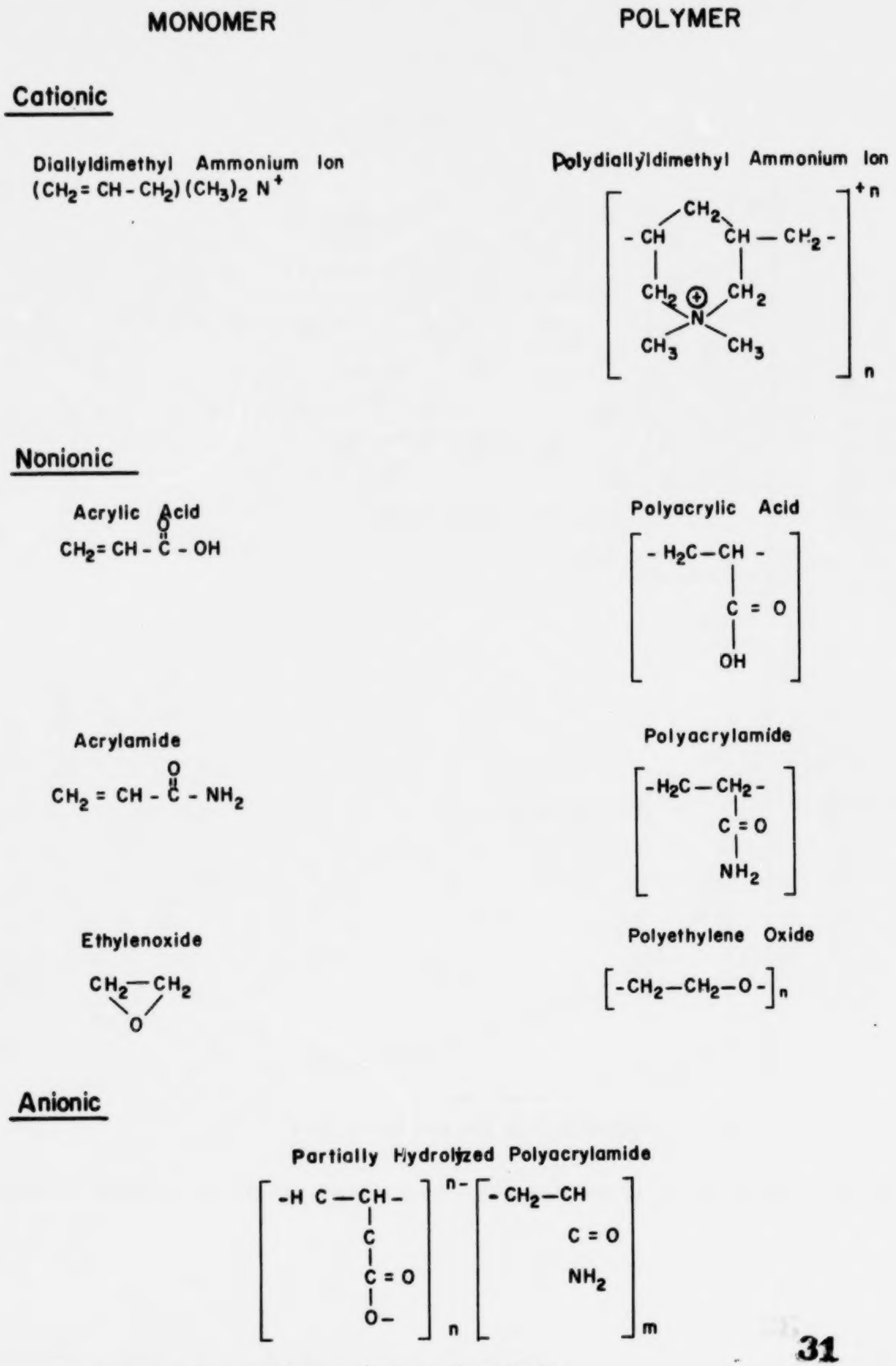
MONOMER
POLYMER
Cationic
Diallyldimethyl Ammonium Ion
(CH2= CH - CH2) (CH3)2 N+
Polydiallyldimethyl Ammonium Ion
Nonionic
Acrylic Acid
Polyacrylic Acid
Acrylamide
Polyacrylamide
Ethylenoxide
Polyethylene Oxide
Anionic
Partially Hydrolyzed Polyacrylamide

Fig. I Structure of Polymers used as Coagulants

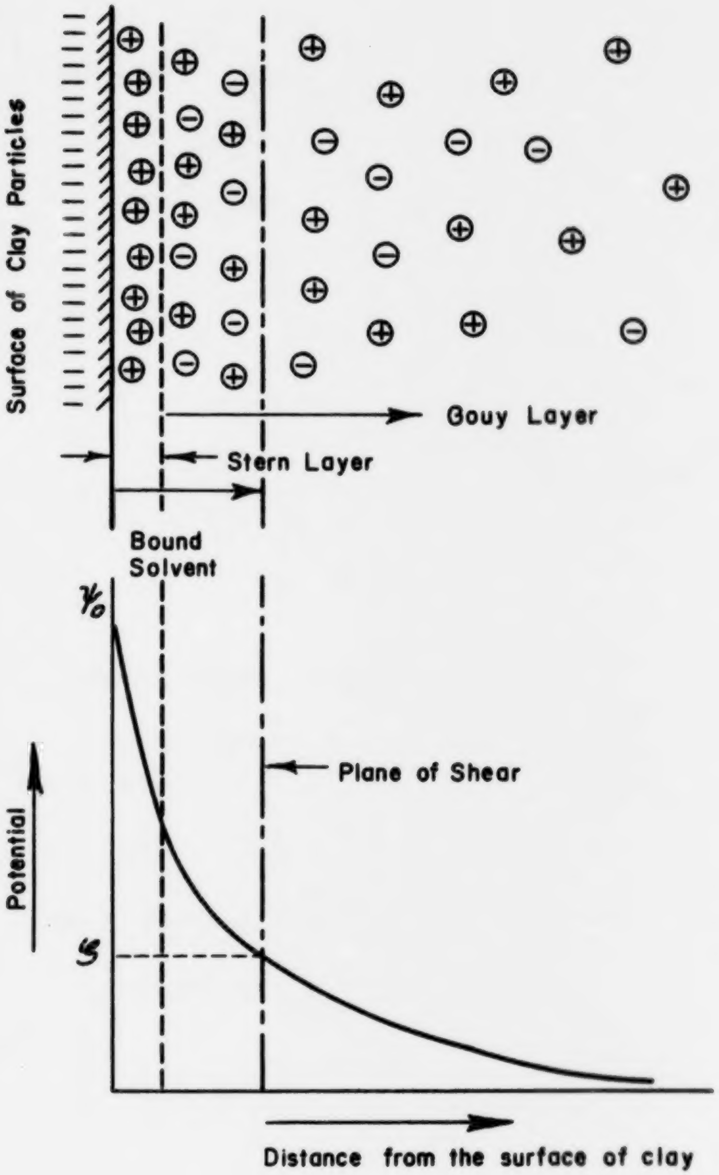
Surface of Clay Particles
Gouy Layer
Stern Layer
Bound Solvent
ψ_0
Plane of Shear
Potential
ζ
Distance from the surface of clay

Fig. 2 - The Structure of the Stern-Gouy Double Layer and the Corresponding Potentials.

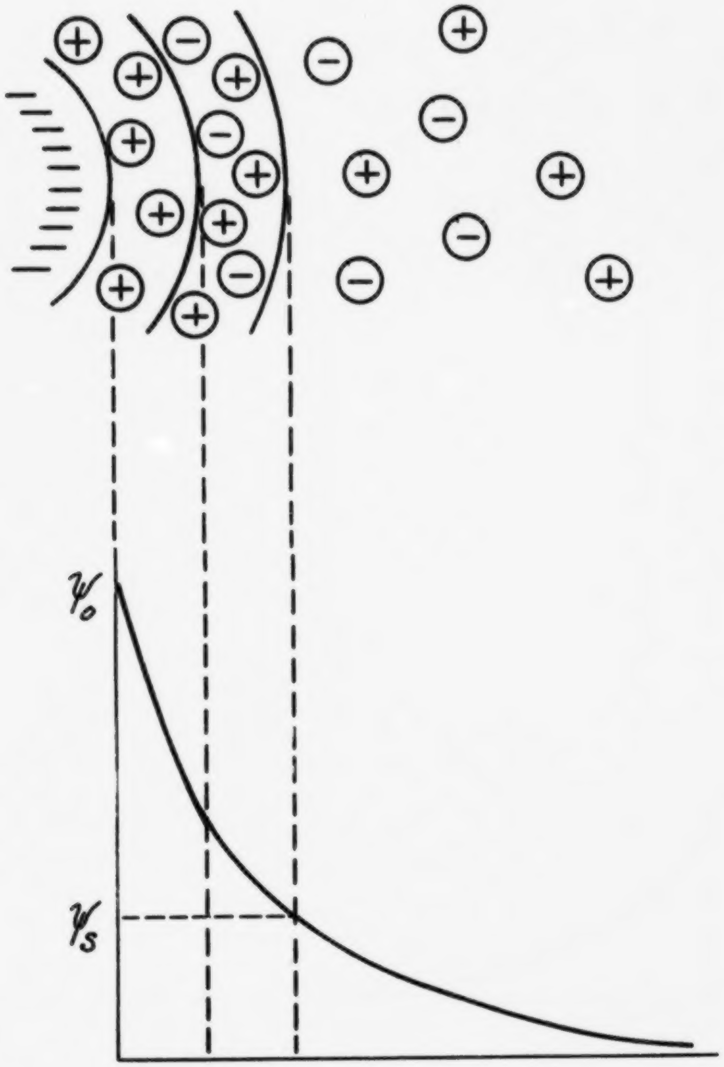

Fig.3 - Effect of high concentration of monovalent ions on potential distribution

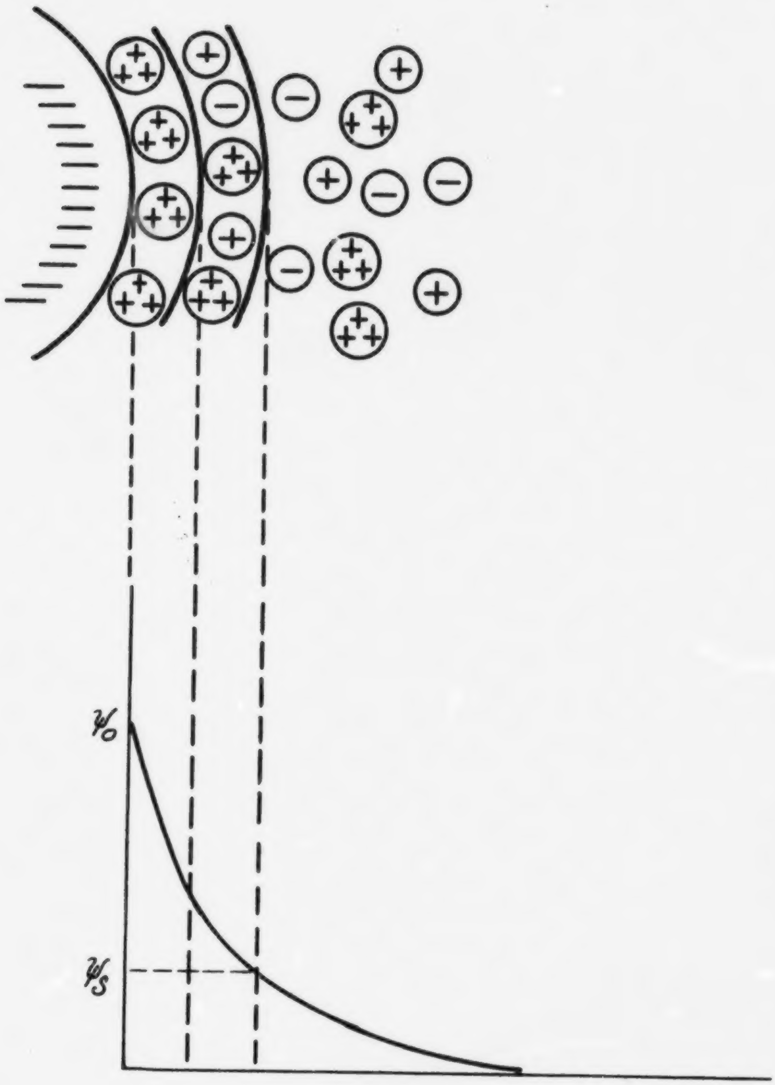

Fig. 4 - Effect of the presence of trivalent positive ions on potential distribution

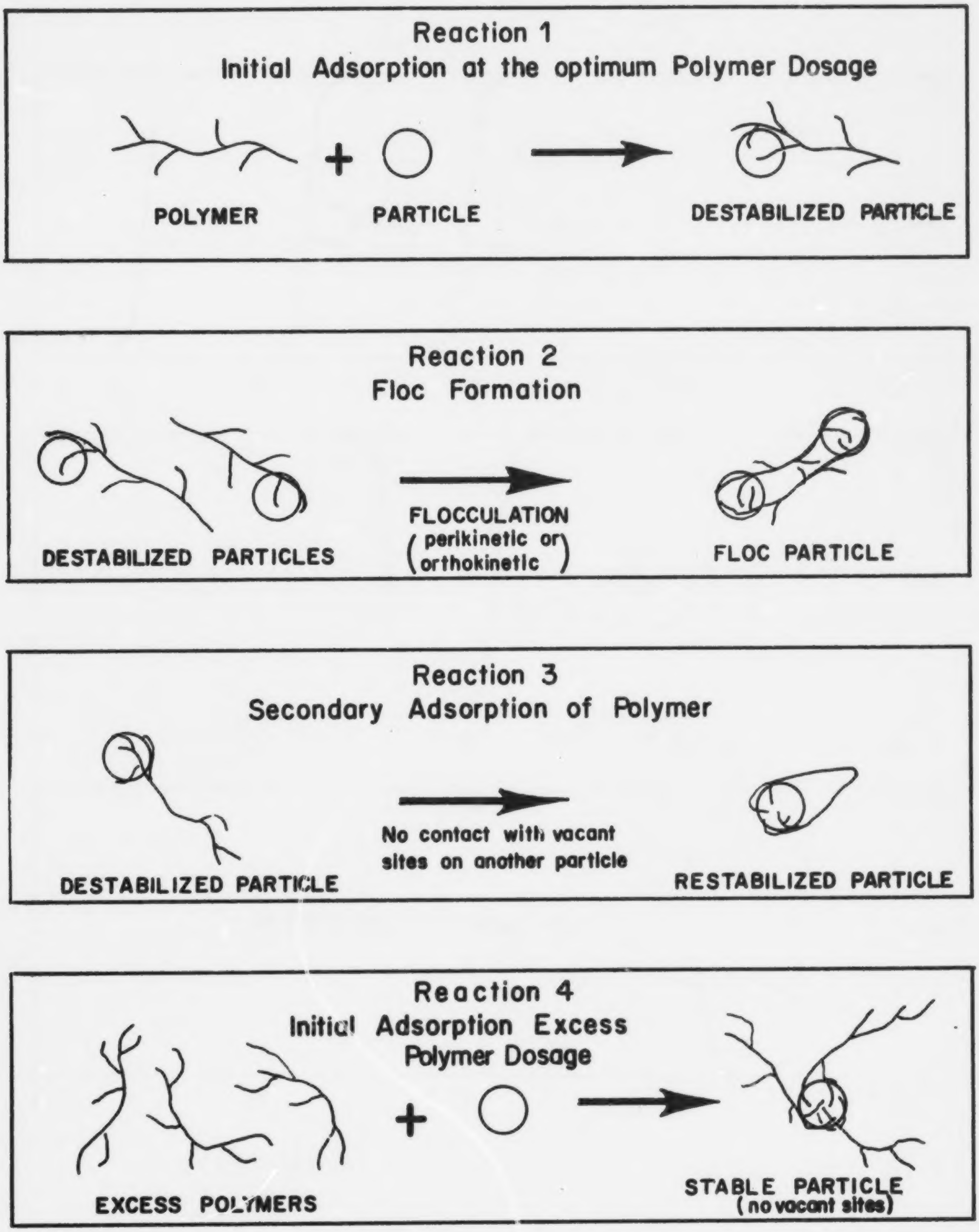
Reaction 1
Initial Adsorption at the optimum Polymer Dosage
POLYMER
PARTICLE
DESTABILIZED PARTICLE
Reaction 2
Floc Formation
DESTABILIZED PARTICLES
FLOCCULATION
(perikinetic or orthokinetic)
FLOC PARTICLE
Reaction 3
Secondary Adsorption of Polymer
DESTABILIZED PARTICLE
No contact with vacant sites on another particle
RESTABILIZED PARTICLE
Reaction 4
Initial Adsorption Excess Polymer Dosage
EXCESS POLYMERS
STABLE PARTICLE
(no vacant sites)

Fig. 5 - Schematic Representation of the Destabilization of Colloids by Polymers

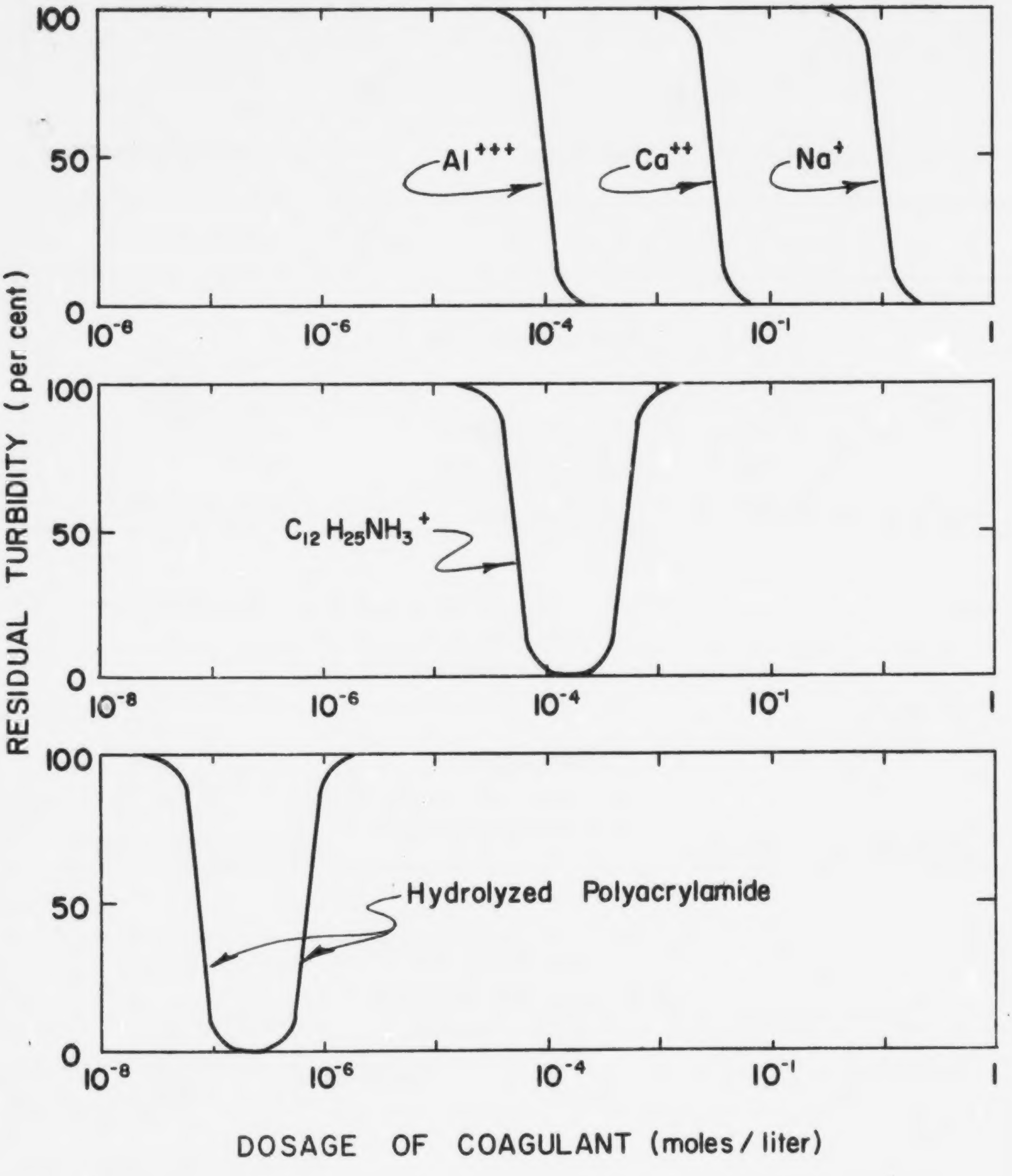

Fig. 6 - Comparison of Coagulation Curves for Several Different Coagulants

HANDLING, STORING, APPLICATION, AND PURCHASING OF WATER SOLUBLE POLYELECTROLYTES

Ronald A. Lo Sasso*

HANDLING AND STORAGE OF DRY POLYMERS

Dry polymers are normally polyacrylamide or hydrolyzed polyacrylamide. These materials are somewhat hygroscopic and care should be exercised in keeping them in an environment which is low in humidity, if at all possible. The material should be stored in the bag in which it is delivered until ready to be used. The bag material should be palletized and kept off the ground.

In the dry form, the material is very stable and can be held for periods in excess of one (1) year, with no detrimental effect. When the material is dissolved in water, the life of the feed solution is very limited and should not be held as a water solution for longer than 24 hours. Due to the very high molecular weight of nonionic and anionic polyacrylamides, there is a normal tendency for the material to revert to its simpler form by breaking of the carbon-carbon bonds. This degradation of the polymer is a function of time, temperature, and the other constituents in the solution water.

Solution water should always be finished water, free of chlorine if possible.

BULK CONSIDERATIONS FOR STORAGE OF POLYACRYLAMIDE AND HYDROLYZED POLYACRYLAMIDE

For large consumers of polyacrylamide, there is always the consideration of obtaining and holding material in bulk. To date, very little has been done and only one or two people, not in the municipal water treatment field, are receiving and maintaining polyacrylamide in bulk silos. Care must be exercised in handling polyacrylamide when large quantities are being stored at one time. The atmosphere in the shipping container as well as the storage container is critical. It should be dry air or dry inert gas at all times. When polyacrylamide is exposed to air containing reasonable quantities of water vapor, the polymer begins to become sticky and lumps begin to form very rapidly. Once exposed to water, the polymer becomes very gummy and is very difficult to dissolve or handle from that point on. Generally speaking, nonionic and anionic polyacrylamides being used as coagulant aids or filter aids are best stored in 25 lb. or 50 lb. bags with only the amount needed being taken from the bag. As stated before, the dry material is stable for long periods, but the solution of this polymer has a very limited shelf life. Care should be taken in choosing the solution water and it should be of the highest possible quality preferably without a high chlorine residual.

LIQUID POLYMERS – HANDLING AND STORAGE

Liquid polymers are normally cationic solutions containing 10% to 60% active polymer. The activity usually depends on final viscosity. This is done both to facilitate handling and because many of these materials cannot be practically dried and then redissolved to for good coagulants. All liquid polymers are sold on an as shipped basis.

Polymers shipped in 55 gallon drums are best stored in their shipping containers. These drums have been chosen by the supplier and contain protective coatings on the steel drums or in some cases, polyethylene liners to protect both the steel drum and the polymer.

Drums should be kept closed at all times when solution is not being taken from them. This is expecially important with some types of polymers which tend to oxidize and become less effective on prolonged exposure to air. The supplier of the polymer should be consulted if there is any question concerning the stability of the product on extended exposure to air.

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*Product Manager, Calgon Corporation

When liquid polymer is being considered, bulk shipment can be advantageous. This is especially true when daily usage approaches 40 to 60 gallons of polymer solution per day.

There are many advantages to bulk shipping and holding of liquid polymers. Normally, there is a price reduction in bulk quantities due to the elimination of the high cost of the shipping container. Freight rates can be established on bulk which are very attractive in comparison to LTL shipment of drums.

Bulk deliveries will be either by truck or by bulk railcar. Shipments by bulk truck should be in trucks with stainless steel, epoxy, or rubber-lined interiors. The supplier should exercise care when using rubber-lined tank trucks in that some materials will penetrate rubber and may leech back into a polymer solution which could contaminate it and make it unfit for potable water applications. All trucks should be thoroughly cleaned prior to loading with polymer. Railcars should be dedicated to polymer service and have corrosion resistant linings. A major consideration in choosing between truck and rail will be size of tanks at the receiving point as well as ability to ship during winter months. Tank truck shipments normally move quickly enough that freezing or exposure of the polymer to severe cold for long periods of time is not a problem. In bulk rail shipments, several weeks may be required to deliver the polymer to the ultimate destination. Water soluble polymers, as they approach freezing, increase in viscosity to a point where they become very difficult to handle. Once frozen, it is very hard to remake a uniform solution without vigorous mixing. Care must be exercised in protecting the polymer solution from freezing during shipment and tank car loading stations should be equipped with a means of heating the tank car if necessary.

Storage tanks at the receiving location should be constructed of either fiberglass, stainless steel, or steel which has been coated with an appropriate protective lining. Piping to and from the storage tank should be either stainless steel, polyvinyl chloride, or similar plastic. Tanks must be protected from freezing either by insulation or by storage inside a heated building.

As we have discussed, freezing is a very real problem with polymer solutions and care should be taken to insure that freezing of the polymer in the storage tank will not occur.

Some polymers have a tendency to air oxidize and provisions to nitrogen cap the storage tank is important if that type of polymer is utilized. The supplier should be contacted prior to final installation of a storage tank and nitrogen capping installed if air oxidation is a problem.

Storage periods for liquid polymers should not exceed one (1) year. Optimum turnover time of bulk tanks is approximately three to six months. Liquid polymers are more prone to degradation even in their concentrated solution and extended storage periods should be avoided.

Tanks should be equipped so they can be easily cleaned. This would include a manhole of sufficient size to allow easy entrance for cleaning. This is especially important if the same tank is going to be used to store different polymers. In many cases these polymers are not compatible and this storage tank should be thoroughly cleaned prior to storage of a new polymer. A 5% sodium chloride solution will aid in removing residual polymer from the storage tank. The tank should be filled with water and sufficient sodium chloride added to obtain a 5% brine solution. The tank should then be mixed either with air or by means of a circulating pump to allow the solution to contact all areas of the tank for a period of two (2) to four (4) hours. The tank should then be drained and thoroughly flushed with water to remove all residual polymer. This concludes the area of handling and storage of polymers, are there any questions?

APPLICATION

1 Polymer dissolving or make down.

2 Holding diluted polymer solutions.

3 Feeding diluted polymer solutions.

DRY

1 Nonionic polymers, maximum solution strength 1%. Anionic polymers, maximum solution strength 1/4%.

2 A suitable disperser should be used at all times to dissolve dry polymers. This is to facilitate the wetting of each distinct polymer particle so that the dry polymer is put into solution as quickly as possible. This also minimizes the tendency for polymer particles to adhere to each other resulting in "fish eyes" in the solution tank. These polymer "fish eyes" are undissolved polymer which will not function as a coagulant aid. "Fish eyes" also have a tendency to plug the feeding system and create high maintenance requirements. The two typical methods of dissolving dry polymers are either by use of an (1) eductor funnel, or (2) vibrating the polymers slowly across a plane of water.

The eductor funnel, as the name applies, incorporates a funnel which is attached to an eductor. Normally, it is advisable to obtain an eductor with a sufficiently large throat so as to reduce the tendency for polymer to plug during the makeup of the polymer solution. The eductor should be cleaned between uses, if at all possible.

Vibrating the polymer across a plane of water is a method which we have found to be very useful in dissolving both small and large quantities of dry polymer.

SLIDE I - Shaker Feeder

SLIDE II - Larger Shaker Feeder

SLIDE III - CPF System

SLIDE IV - BPF System

DISCUSSION OF TYPICAL POLYMER FEED SYSTEM TO FEED FROM 50 TO 200 LBS. DRY POLYMER/DAY (SPECIFICATION ON BPF SYSTEM)

Solution time for dry polymers varies between 10 minutes - 4 hours. This means the dry polymer should be left agitating in the tank for approximately 15 to 30 minutes prior to use. The mixer should be a slow speed, 350 rpm mixer. Once the solution is dissolved it should be transferred, as we have seen in the BPF System, to a feed tank. This allows a second batch of polymer to be made up while the system is being treated without any interruption. If polymer is dissolved in the feed tank, a varying solution strength will occur during the dissolving of the polymer.

Generally speaking, we have found that progressive cavity type pumps such as those sold by Robinson Myers, are excellent for dispensing the diluted polymer feed solution. These pumps have good adjustment from 5% to 100% of capacity and act as very efficient metering devices to insure that only the proper amount of polyelectrolyte is dispensed at any given time. We normally add dilution water on the discharge side of the pump to further dilute the polymer and to enable it to be properly mixed with the raw water as quickly as possible.

LIQUID POLYMERS

Liquid polymer are normally cationic in nature and are shipped as solutions . some type of basic cationic approved material. Generally speaking, these materials are not suitable for drying and due to the larger quantities of cationic polymers normally used, especially where the product is being used as a primary coagulant, the polymer manufacturers have supplied cationic polymers for municipal water treatment only in liquid form. These materials come in varying concentrations and varying viscosities.

Some materials have very low viscosity on the order of 10 to 100 centipoise. Other polymers have higher viscosities on the order of 1000 to 5000 centipoise.

In designing a liquid bulk storage and dilution system, it is best to design around the most viscous material since with such equipment, you can easily handle more dilute solutions. However, it can be very difficult to take a system which has been disigned to handle very low viscosity material and adapt it too much higher viscosity materials.

Liquid polymers as we have discussed, can be delivered in either 55 gallon drums or in bulk quantities. Normally, when the material is shipped in drums, a quantity of the polymer is removed and added to a tank where the dilute feed solution is prepared. When bulk storage is anticipated, a suitable pump should be used to transfer the concentrated polymer to the make-down tank. The amount of polymer dispensed can be determined by taking a pump of known output and running it for a predetermined period of time. An alternative method would be to gauge the tank and add a known quantity of polymer based on calibrated tank.

Normally, we try to dilute the cationic polymer to such a point that it is easy to handle and gives a good workable feed solution. Normally, the concentrated polymer is diluted approximately 10-20 to 1 with solution water. This should be allowed to mix for at least several minutes and then transferred to a second tank which will be used as the feed tank. This allows you to make a second batch of polymer without affecting the concentration on the material being fed to the water system.

The same type of metering pump is recommended for solutions of cationic polymer. Solution water on the discharge side of the pump is optional in that the cationic materials are generally faster acting and are added into areas with sufficient mixing to insure that the polymer will effectively destabilize the colloidal suspension. We have found that the success of a polymer application often is as dependent on the proper feed system as it is on the mechanics of the system to be treated and the organic polymer being chosen. A proper polymer feed system is critical to properly evaluate the organic polymer and to provide the lowest ultimate cost to the water treatment plant. Dry polymers must be dissolved properly and fed carefully to insure maximum performance at minimum cost. Cationic polymers, since they are sold in a liquid solution, are easier to deal with. However, since larger quantities normally are being fed, a system capable of supplying the proper volume of polymer at all times is critical. I cannot stress too strongly the point of having an adequate feed system for feeding organic polyelectrolytes.

PURCHASING OF ORGANIC POLYMERS

There are, to date, many organic polymers available for sale to municipal water treatment systems. The nonionic and anionic polymers are all based on acrylamide as the starting monomer. Due to the variations in polymerization technology, however, these polymers differ in effective molecular weight and thus performance. Polymers, in my opinion, can not be standardized and in order to purchase even nonionic and anionic polymers intelligently, evaluation of the product in laboratory and full plant trial is mandatory. With cationic polymers, the problem is even more acute since there are two basic types of cationic polymers sold to the municipal water industry. One is based on a quaternary ammonium type compound where all others are based on polyethylene imine. These materials are as different as night is from day, and only be actual evaluation in the system to be treated, can true performance data be generated.

I recommend strongly that in evaluating polymers, the following scheme be utilized so that a purchase arrangement can be arrived at which is the most equitable for the municipality and the fairest to the polymer manufacturer.

Laboratory tests should always be conducted to determine the feasibility of polymer application to a specific municipal water system. Based on this laboratory evaluation, a full plant trial should be conducted with polymer dosage being monitored very carefully. Raw water turbidity, settled water turbidity, and the filterability should be measured along with any other parameters a specific plant uses to determine the effectiveness of a given coagulant. This data should be tabulated against dosage and a dosage versus performance curve generated. With this curve, and a price for the specific polymer, the cost to treat one (1) million gallons of water at a specific performance can be determined very easily. By doing this for several organic polymers, a comparison of polymer at a specific performance level can be determined. Since polymers vary in nature and concentration, it is possible to purchase organic polymers with a price range varying from as low as 20¢/lb., for some types of liquid cationics to as high as $2.25/lb., for some dry nonionic and anionic materials. With such a varying price structure, and a varying dosage versus performance curve, it is impossible to evaluate organic polymers simply on price. Only by generating a true dosage versus a performance curve, can a fair evaluation be made based on a comparison of several polyelectrolytes. With this performance versus dosage curve, a bid can be drawn up showing varying amounts of polymer to treat a given volume of water. The quantities of each polymer may vary, but the volume of polymer to treat a given quantity of water and to obtain a constant degree of performance can be fairly computed.

USE OF POLYMERS AS A PRIMARY COAGULANT

BY

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USE OF POLYMERS AS A PRIMARY COAGULANT

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INTRODUCTION

The term primary coagulant offers little definition as to where and how polymers are used in the initial unit treatment processes of water treatment and as to how system performance is improved by their use. It is to these perspectives, and particularly to the aim of developing guidelines for the design and operation of treatment systems using polymers as primary coagulant, that this discussion has been developed.

When one is considering coagulation, the success of the coagulation effort is inextricably associated with the performance of the primary separation process following the coagulation and flocculation (or conversion) processes. In viewing the conversion and separation process sequence;

- The conversion step is intended to effect the conversion of dissolved and colloidal materials to destabilized forms that are separable in typically-used sequential separation processes such as gravity sedimentation or contact flocculation.
- The conversion may be effected in zones of gentle agitation subsequent to rapid mixing or, as in the case of filtration, in the stream either prior to or during filtration.
- In either case, the success of the combined conversion/separation process system, from an operational viewpoint, lies in maximizing the usefulness of the omnipresent variant of filtration following gravity sedimentation.

Within this overall framework for conversion/separation, there exists many alternative approaches to chemical pretreatment in the water treatment field. Polymers represent but one form of chemical additive for enhancing/effecting the conversion step. Historically, aluminum and ferric or ferrous salts were first used to effect conversion, followed later by variants of lime softening techniques developed to provide acceptable water hardness levels as well as pretreatment for clarification. In the last few decades, the role of polymers has been discovered, refined, and developed to the extent that, at present, a flood of diversely-named and chemically-structured compounds are now available, multiplying many times the traditional roster of chemical pretreatment alternatives available for catalyzing or enhancing the conversion step. Needless to say, from both a design and operational perspective, the addition of polymers as a chemical pretreatment alternative should, with the appropriate transfer of information from the researcher to the designer, the designer to the operator, and from the regulatory authority back to each of the preceding, result in a reduction of many of the traditional problems facing the water treatment industry.

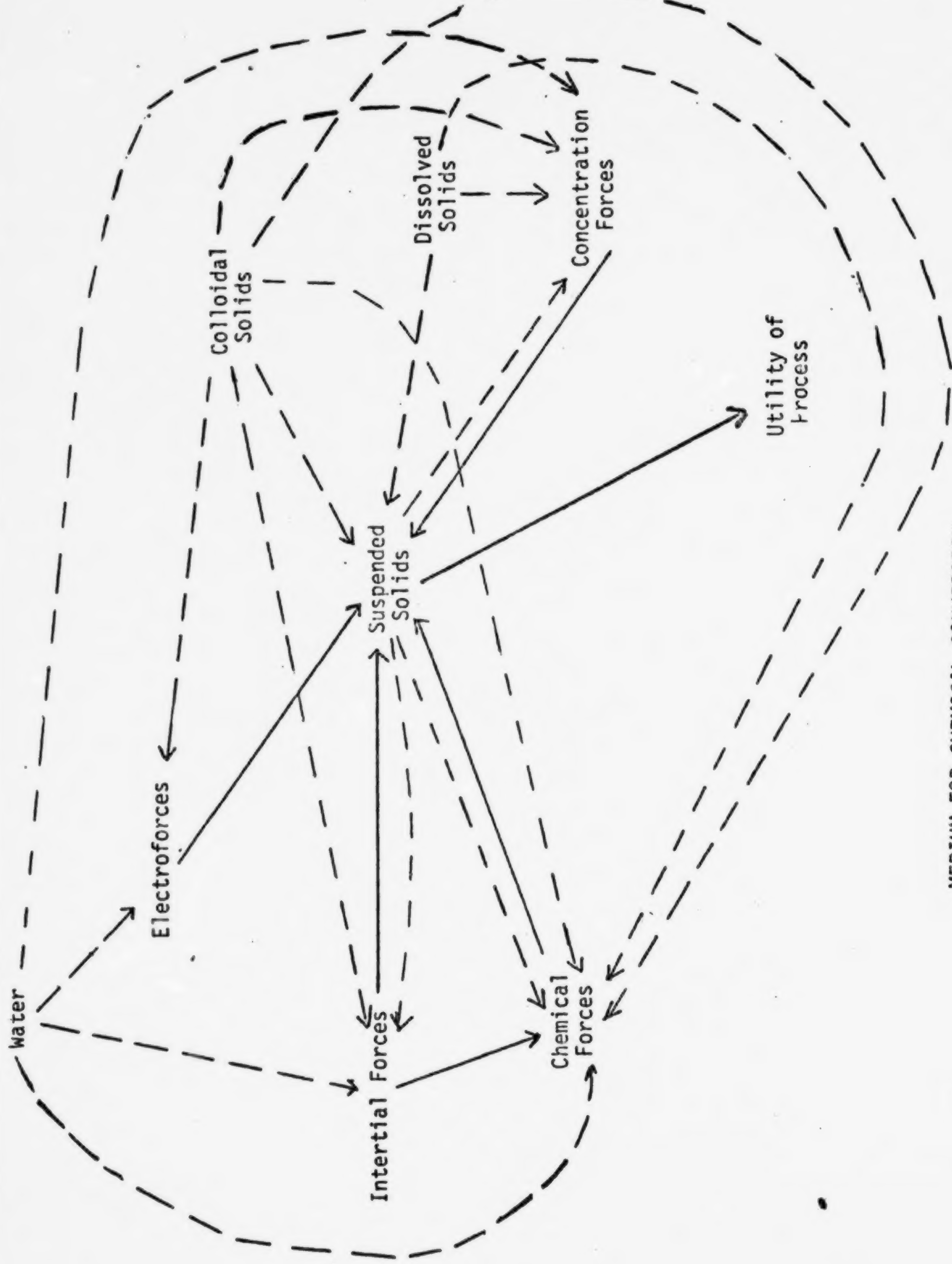
Unfortunately, such has not been the case. As one reviews the wealth of experience in the field, it is apparent that, even with the evolution of conversion/separation process understanding to its present status, there exist critical gaps between the researcher, the designer, and the operator with respect to sufficient overlap of understanding, such that the knowledge and experience of each can be integrated to improve general, rather than situation-specific, understanding of conversion/separation. There has been a general inability of the researchers, users, and operators of the various water treatment processes to develop information transfer techniques which permit the experiences and information gained in one situation or application (be it in the laboratory or at a water treatment plant) to be beneficially applied in the next circumstance. The conversion-oriented processes are better understood than are the separation processes upon which the success of the former must ultimately be measured (Reference 1). At present there exists no capability to predict the nature or extent of solids separation which will occur in a water filtration process, and one approaches, in the absence of pilot process data, the prediction of separation which will be obtained with considerable caution. The absence of any perceived economic benefits to be derived from understanding the processes, and the strong consistency in the applications orientation (eg, rapid sand filters following specific types of pretreatment), have made duplication a feasible method for design and operation. Success in this approach has generated a complacency and vested interest on the part of the designer, operator, and regulatory authority, and, with few exceptions, attempts at developing empirical or rational approaches to design have been outside the main boundaries of applications of the processes. The pressure for rationalization of the rapid sand filtration process has resulted from the demand for ever-increasing throughput rates, and it appears quite likely that the rapid sand filtration process will be replaced by the dual media filtration process before a rational technique is developed to describe its design and operation. And, unless the conceptual approach to considering filtration processes is radically altered, it does not appear that there will be any significant gains made in developing rational techniques for designing and operating these more advanced filtration processes.

THE MECHANISTIC APPROACH

The mechanistic approach to dealing with understanding of the conversion/separation processes has dominated all efforts towards rationalizing process behavior, and it appears appropriate, in view of the preceding, to examine the contribution of this approach in assessing ways to close the gaps between researcher, designer, and operator interests associated with these processes.

It is important, first, to consider the commonalities of the physical-chemical environment, or the *medium,* for chemical conversion, and to establish from this a perspective for synthesizing the basic knowledge gained to date. The medium (Figure 1) is comprised of mechanisms and components, each operative at different levels. The components of the medium consist of water, and suspended, colloidal, and dissolved forms of solids, and the mechanisms are those variously related to electro-forces, concentration forces, inertial forces, and chemical forces. The solid arrows of Figure 1 define mechanistic interactions, and the dashed arrows define component interactions, the aggregate of the interactions in any given medium serving to define the utility of the mechanisms for any specific application.

The assumptions associated with this diagrammatic presentation are as follows:


Water
Electroforces
Intertial Forces
Chemical Forces
Colloidal Solids
Dissolved Solids
Concentration Forces
Suspended Solids
Utility of Process

MEDIUM FOR CHEMICAL CONVERSION

FIGURE 1

- All mechanisms described in the literature for accomplishing the transport and attachment of particles are valid and operative at levels determined by the components of the medium, and the interactions between the components.
- The interactions between the mechanisms and components are desirable and can be determined.
- The effectiveness of the mechanisms and components can be integrated.
- Within this framework, all of the existing knowledge has a level of applicability in predicting the behavior of primary coagulants in a primary separation.

Needless to say, the application of the preceding perspective to understanding the behavior of polymers as primary coagulants is not easily implemented with the results attained to date by the mechanistic approach. That is, the present orientation of this approach is towards analysis of the individual mechanisms rather than to synthesis. The mechanistic approach has as its basic objective the development of rational understanding of the associated individual processes such that they can be designed and operated using basic system data and/or information. Emphasis is placed on the *why*, not the *how*, the former requiring differentiation and the latter requiring integration. The mechanistic approach has over-emphasized the use of pilot systems to simulate the real thing rather than emphasizing the definition of the *boundaries* of various possible mechanisms which permit specification of the process.

Another facet of the mechanistic approach is the continual consideration of smaller and smaller elements of the problem, with no assurance that the understanding of the details of the process at a very disaggregate level will aid the understanding of the total process. The latter can be assessed only when the various expressions defining the process elements at the disaggregate level are integrated to synthesize the total process. Thus, for example, the contribution which the understanding of the electrokinetics of filtration will have on the understanding of filtration has yet to be defined.

One can generate reasonable and valid arguments for the case that we have reached the point of counter-productivity in our efforts to understand the conversion/separation processes, particularly when assessed in terms of synthesizing the performance of the filtration process. The greatest indication of this counter-productivity is the limited impact of much of the research on design and operation. The resulting body of knowledge does not seem to result in any amplification of effort. That is, the field appears to be in the position where one piece of research leads to two additional research efforts. It would be expected, based on the volume of work done to date, that the point would have been reached where each piece of research would explain and make available large portions of the existing information base. The fact that this is not happening suggests that either the *critical mass* of information has not been attained or that the general framework in which the work is being done is insufficient. Which of these more nearly describes the circumstance cannot be fully determined until a synthesis context for information transfer is developed; however, there are strong indications that it is the framework which is not sufficient.

In order for a framework to be sufficient to permit the development of a unifying concept of the conversion/separation processes, and the role of polymers therein, it is necessary that the processes be examined and studied independent of particular applications. This will require the development of a perspective for investigating and dealing with the conversion/separation *process train* as an entity, in which a high priority is placed on the use of information to provide a synthesis of the process train rather than on a continuing emphasis on individual process analysis, i.e., to unify the relative impact of all process variables (including operator skill) in a manner which provides answers to design and operating questions within a commonly accepted perspective for defining and dealing with problems.

RESPONSE SURFACE CONCEPT FOR PROCESS UNDERSTANDING

The response surface concept for process understanding has been developed to create a perspective of how individual process variables, as understood by research, design, operating, and regulatory groups, affect the performance of a unit process or process train. This concept, originally developed in a study of the dissolved air flotation process (Reference 2), offers significant promise as a framework for advancing the understanding of the conversion/separation processes in water treatment, in that individual response surface (relating a performance parameter with an individual design or control variable) can be integrated or unified to identify for the designer and the operator the range of process variables in which desired performance and operating characteristics can be obtained.

The typical response surface exhibits peaks, valleys, and low and high plateaus in different dimensions (Figure 2), where a peak or high plateau is associated with high process efficiency in that dimension. A high plateau on the response surface in a number of dimensions is indicative of a region of stable and high process performance, i.e., of a region of process variables in which little change in process efficiency occurs for large changes in the process variables, in which case the process will not be difficult to operate. On the other hand, process location on a steep slope of a response surface will result in an unstable process that is difficult to operate at a desired level of performance. Thus, as a general goal in process or process train design, it is desirable to attempt to locate the process at a point on the response surface which will occupy the ridge or high plateaus on the response surface in a number of dimensions.

A number of the dimensions in the "space" in which response surfaces are constructed may not be explicitly quantifiable, eg, level of operator skill required, operating flexibility required under projected raw water loads, etc. Nonetheless, such dimensions are valid factors to be considered in a specific design, particularly from the operational perspective, because of the relationship between process efficiency and mode of process operation.

Because the response surface concept deals with the question of feasible regions of operations, and process performance stability, some degree of measure can be placed on the traditionally non-quantifiable dimensions insofar as these dimensions of an overall response surface can be broken down into finite steps to which quantifiable measures are associated. Alternatively a design can be developed in a region of the response surface wherein process stability is attainable to the extent that the potential impact of the non-quantifiable dimensions on process performance is reduced.

The use of the response surface as a basis for establishing a treatment system design and/or operating objectives for a functional treatment system differs from the traditional "point" design or operating approach, in which a single set of guidelines based only on historical practice are used. Often the historical data base, specific to other applications, is incomplete, and was developed in consideration of objectives no longer relevant in terms of a new situation. In contrast with the "point" approach, there is no need for an *a priori* decision as to the quantity to be maximized or minimized when using the response surface concept, i.e., the ramifications of moving from any one point on the response surface to another can be analyzed in terms of the trade-offs involved in several performance parameters. For this reason, response surfaces relating performance efficiency and process variables at one scale can be related to those at the next scale (laboratory scale pilot scale prototype scale) as a basis for predicting process performance, eg., by comparison of jar test results with pilot or prototype-scale results to develop a judgmental basis for predicting prototype performance on the basis of jar test results.

APPLICATION OF RESPONSE SURFACE CONCEPT TO CONVERSION/SEPARATION

The characterization of a unit process or process train can be approached from any of several levels of investigation, depending on the specific information requirements for the inquiry. These levels are typically identified as molecular, particle, subprocess, or process, where, eg., study at the molecular level may deal with the impact of van der Waal's forces on process behavior, and investigation at the process level may use only the broadest measures of input and output to characterize process performance. The present commentary is addressed to the subprocess level and, because the efficiency of the conversion processes are measurable only in terms of the performance of the primary separation process, both primary conversion (coagulation and flocculation) and primary separation (sedimentation) processes are considered.

The initial step in applying the response surface concept entails defining the significant parameters that can be used to effect control and to describe the probable performance of the coagulation-flocculation-sedimentation process train for treatment of raw waters. The selected parameters can then be used to formulate a set of response surface relationships that can be used to define a design or operating point in terms of the design and control variables and a performance level associated with the point.

Establishment of Parameters

The parameters associated with the coagulation-flocculation-sedimentation process train (at varying degrees of importance) are the following:

- Dissolved solids - type and concentration
- Colloidal solids - type, concentration, and degree of surface activity
- Suspended solids - type, concentration, and degree of surface activity
- Chemical dose - type, concentration, and degree of surface activity
- Mixing and flocculation energy input rates and duration of input
- Separation - time and type of separation

- pH
- Temperature

In the absence of an explicit parameter set for the preceding, several implicit measures are usually selected as operationally observable measures of the potential for conversion/separation:

- Colloidal and suspended solids in the influent stream
- Influent stream flow rate

A third factor requiring parameterization is the effectiveness of the chemical conversion processes initiated as a result of chemical addition. Typically the jar test procedure is used to simulate the sequence of material and energy transfers and the physio-chemical environment that is expected in the pilot or prototype system, i.e., to simulate the rapid transfer of chemicals into the flow; the transfer of energy into the flow to effect flocculation; and the separation of the converted solids. The jar test procedure is commonly selected not only because of its broad acceptance for this purpose, but also because of the lack of an acceptable alternative for laboratory-scale testing. The chemical doses ascertained by the jar test procedure may not apply to specific situations, but relative shifts in supernatant quality with changing dose patterns in the jar tests are commonly interpreted as indicative of similar shifts in chemical doses necessary to accomplish solids separation.

Chemical Behavior

The inherent behavior patterns of polymers differ widely from those of the inorganic and metal ion coagulants used in the conversion step. The general effect of increasing the doses of lime or metal ion coagulants beyond "optimal" levels is that of forming "blankets" that remove particles by a physical sweeping as the blanket is settled. Thus the use of excess dosages of these chemicals has the advantage of stability, i.e., performance remains stable or increases slightly with increasing dose beyond a minimal dose level. Because of this performance characteristic of lime and metal ion coagulants, it is possible for an operator to correct an under-dosing situation by shifting to an over-dosing situation, and then backing off gradually to an optimal dose without upsetting the performance of the conversion/separation system.

Polymers exhibit a much different behavior pattern than is shown by the lime and metal ion coagulants. Polymers typically have helical molecular structures comprised of carbon chains with ionizing groups attached. These radicals ionize in solution to effect a straightening of the chain by electrical repulsion. Colloidal solids can then interact with the straightened chain by electrical interaction and absorption; as the charges neutralize, the polymer starts to coil again, eventually forming a large enough floc to be susceptible to removal. A basic problem with utilization of polymer is that an overdose leads to an excess of charged sites being present in the aqueous solute such that they cannot be neutralized. In this case the straight chain structure is maintained, the system can become highly stable, and there is a diminished level of removal effected. That is, in terms of a response surface relating performance and polymer dose:

- Polymers have definable upper and lower dose boundaries which, if exceeded, will result in a deterioration of performance.

- The range of application of polymers must be controlled within these boundaries if the polymer treatment is to be effective.

Given the preceding response characteristic for polymers, it is apparent that there exists, in a prototype operation, no margin for error in selecting a polymer dose. The operator does not have the option of simply overdosing with polymers as an interim corrective measure as he does with the lime or metal ion coagulants. Because of the time delay between the addition of polymer at selected dose in the conversion processes, and the development of information on the quality of effluent from the separation process that is required to assess the efficacy of the polymer dose, the *a priori* selection of an incorrect polymer dose will require several hours of operation to elute the improperly dosed flow from the conversion/separation processes, during which time the operator must ascertain whether to increase or decrease the polymer dose to attain the desired process train performance. At this point, the only tool available to an operator for making this decision is a jar test-scale response surface relationship (Figure 2) between a supernatant quality measure and polymer dose.

Conceptualization of Response Surfaces

Control and Process Variables

The foregoing information can be used to select the appropriate parameters for characterizing the performance of a conversion/separation process train, and to postulate the shape of the response surfaces associated with changes in the parameters. The control variables available at the time the design is conceptualized are as follows:

- Mixer velocity gradient

- Flocculator velocity gradient

- Specific chemical type and dosage

- Point of chemical addition

- Clarifier configuration, surface loading rate, weir loading rate, and sludge withdrawal rate

The above set of variables is not the only one which can be used to define the conversion/separation process train in terms of variables; however it is sufficient in scope to permit a conceptual specification of a design. From another perspective, that of operating a functional treatment plant, the number of variables in the control matrix is reduced significantly by the "fixed" nature of the design, leaving typically as control variables only:

- Mixer velocity gradient

- Flocculator velocity gradient

- Specific chemical type and dosage

RESPONSE SURFACE RELATIONSHIPS
FOR TYPES OF CHEMICALS
USED IN CONVERSION/SEPARATION

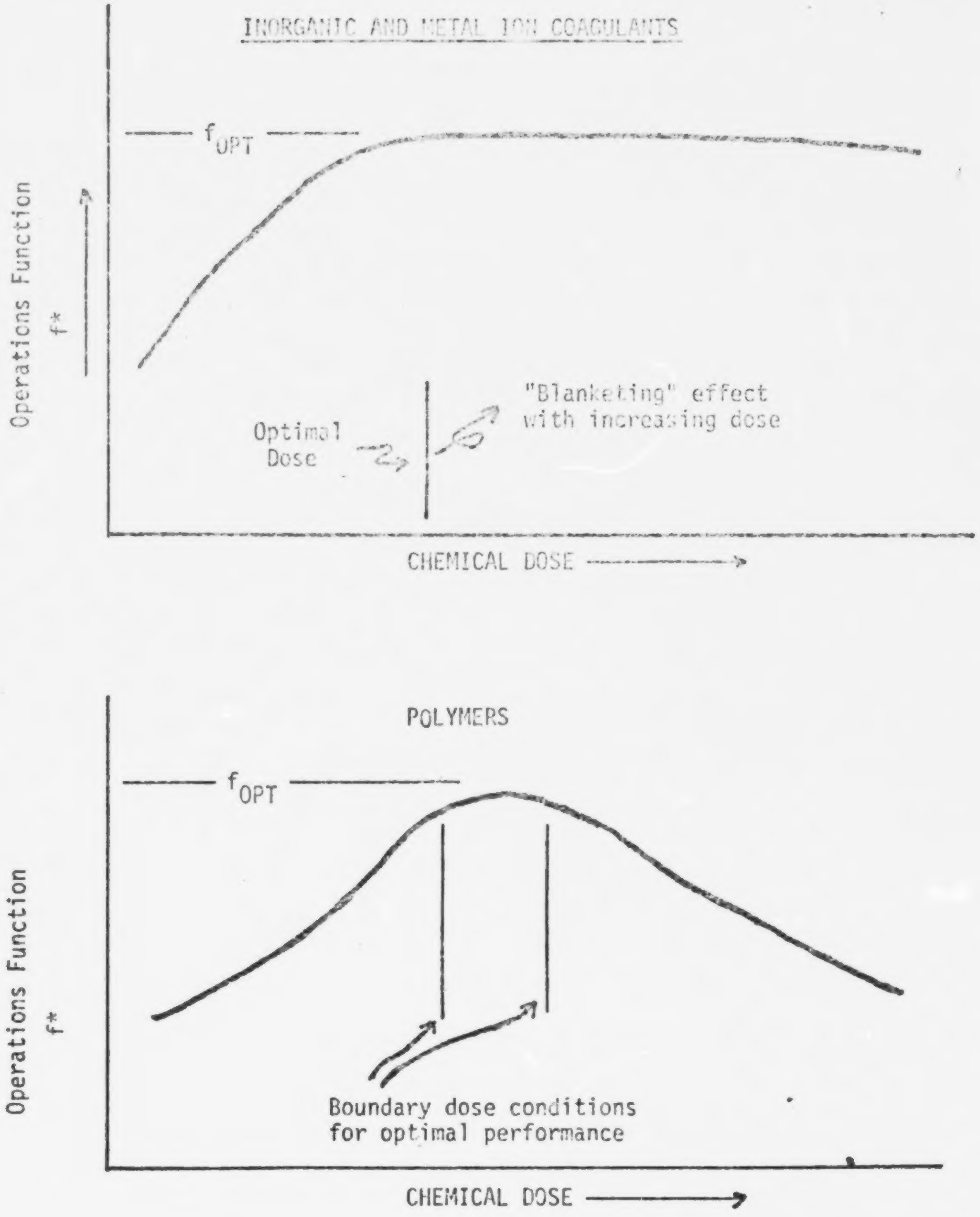


FIGURE 2

The selection of criteria for process performance is dependent upon the objectives for the process train as applied in the field. Inasmuch as the value of a performance variable depends upon the sampling and analytical methodology used, the methodology should be done with reference to the function to be served, alternative functional goals being:

- Maximization of clarification
- Optimizing the character of the effluent solids for removal by a subsequent filtration process

Among alternative performance variables which could be selected for evaluating the performance of the conversion/separation process train are: suspended solids removal, turbidity removal, removal of bacteria, algae and viruses, and removal of oxidized metal ions. Additional parameters that may be of concern are hardness and phosphate removal and final pH. A typically selected performance variable is the removal of suspended and colloidal solids as measured by turbidity.

Development of Response Surfaces

A basic functional equation defining a mathematical model of the conversion/separation process train can be represented (using selected of the above variables) as:

$$f = \frac{X_I^S - X_E^S}{X_I^S} = f^* \left(G_M, G_F, LLR_C, X_I^S\right) \qquad (1)$$

where:

f = Efficiency of removal of colloidal and suspended solids as measured by turbidity

X_I^S = Influent turbidity (of stream entering the conversion process)

X_E^S = Effluent turbidity (of stream leaving the separation process)

G_M = Mixer velocity gradient

G_F = Flocculator velocity gradient

LLR_C = Clarifier surface loading rate

f^* = "Operations" function that is related to specific chemical type and dosage

In this context, any one point in four dimensional space represented by a given combination of G_M, G_F, LLR_C, and X_I^S may be considered as a potential design point, in that these four parameters are assumed to determine the design criteria for the required liquid handling and energy transfer systems.

The remaining variables to be resolved in the design are incorporated in the design operations function, f*. For any one design point, multiple values of f are possible depending upon the value of f*. One maximum value of f can be defined which must occur at the optimal operating conditions for a particular design point, such that

$$f_{OPT} = f^1 \, (G_M, G_F, LLR_C, X_I^S) \qquad (2)$$

where:

f_{OPT} = Maximum removal efficiency

f^1 = Optimal operations function

Inasmuch as it should always be possible, through some set of trial and error procedures, to determine an optimal combination of the above control variables, the function of Equation 2 is significant and can be used to define maximum process performance. It therefore remains to speculate on the response surface defined by the conversion/separation process train when expressed in six-dimensional space (the dimensions relating to the four control parameters in the design point, the operations function, and the performance parameter).

Probable Shapes of Response Surfaces

The anticipated shapes of the response surfaces can be obtained by speculating as to the probable behavior of the chemicals and the various subprocesses. This is most readily done by assuming the independence of each of the subprocesses which in an experimental context entails holding all parameters except one constant, and defining the shape of the performance curve for the varying parameters.

The probable shapes of the response surfaces for chemical behavior as defined in a preceding section are shown in Figure 2. The relationships shown in Figure 2 can be described as follows:

- For inorganic and metal ion coagulants: the performance measure increases at a decreasing rate to an optimal dose, above which little change in the performance measure occurs with increasing dose.

- For polymers: the performance measure increases with increasing dose to a maximal level in an optimal dose range, above the upper boundary of which the performance measure decreases with increasing dose.

The two response surface relationships of Figure 2 can be combined into a single response surface (Figure 3) to illustrate the response contour associated with a combined inorganic or metal ion coagulant/polymer chemical dose pattern. In the format of Figure 3, the response surface relationships can be used to indicate the relative tradeoffs in the performance measure attainable by shifting chemical dose in any of three patterns, i.e.,

COMBINED RESPONSE SURFACE RELATIONSHIP FOR CHEMICAL DOSAGES IN CONVERSION/SEPARATION

Note: Contours as f*

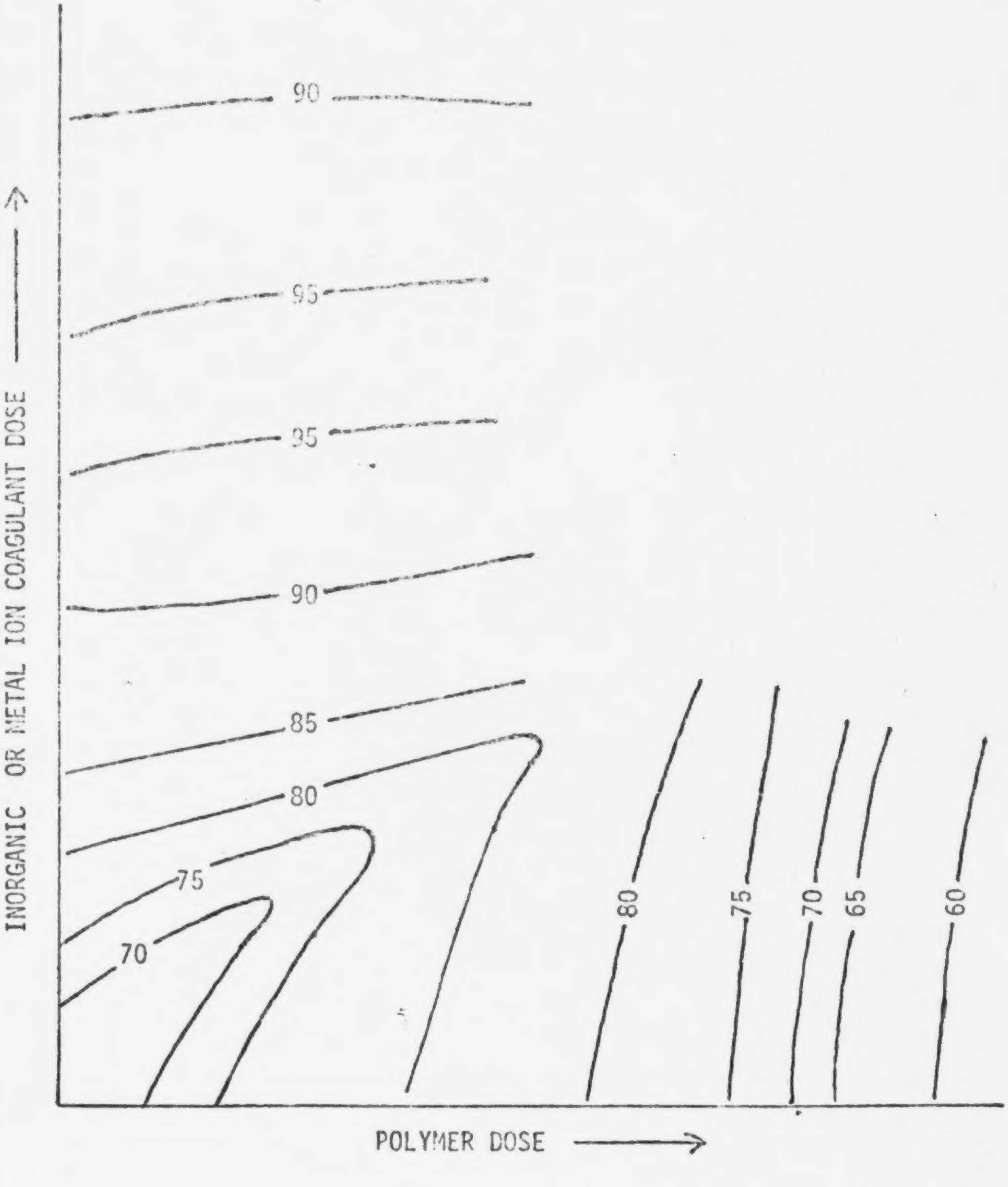


FIGURE 3

- Changing polymer dose at a constant inorganic or metal ion coagulant dose.

- Changing inorganic or metal ion coagulant dose at a constant polymer dose.

- Changing the doses of both types of chemicals.

The probable shapes of response surfaces for the control variables G_M, G_F, LLR_C, and X_I^S are illustrated in Figure 4, using the relationship of Equation 2. In reference to Figure 4-a (LLR_C), a maximal removal is expected at an LLR_C of zero, the removal decreasing with increasing LLR_C as shear forces increase and clarifier tank hydrodynamic stability decreases with increasing LLR_C.

The basic application of the conversion/separation processes in the water treatment field is that of removing solids from dilute solutions. To this end it is anticipated that the effectiveness of the process will increase at a decreasing rate (Figure 4-b) as the influent colloidal and suspended solids concentrations increase.

The impact of varying G_M on the performance measure relates to providing the necessary energy for uniformly distributing the chemicals at the point of chemical addition. The response of the performance measure (Figure 4-c) is expected to increase at a decreasing rate with increasing values of G_M to a peak or saturation level (Figure 4-c). Beyond the saturation level, it is not anticipated that performance of the rapid mix system will change significantly with increasing values of G_M.

The impact of varying G_F is two-fold, relating both to providing sufficient turbulence for the growth of floc and to avoiding the shearing of the floc once formed. The response of the performance measure with increasing G_F (Figure 4-d) is expected to reach a peak or saturation level, followed by a decay in performance with increasing G_F values as a result of increasing turbulence and the associated shearing of floc.

Utilization of Response Surfaces

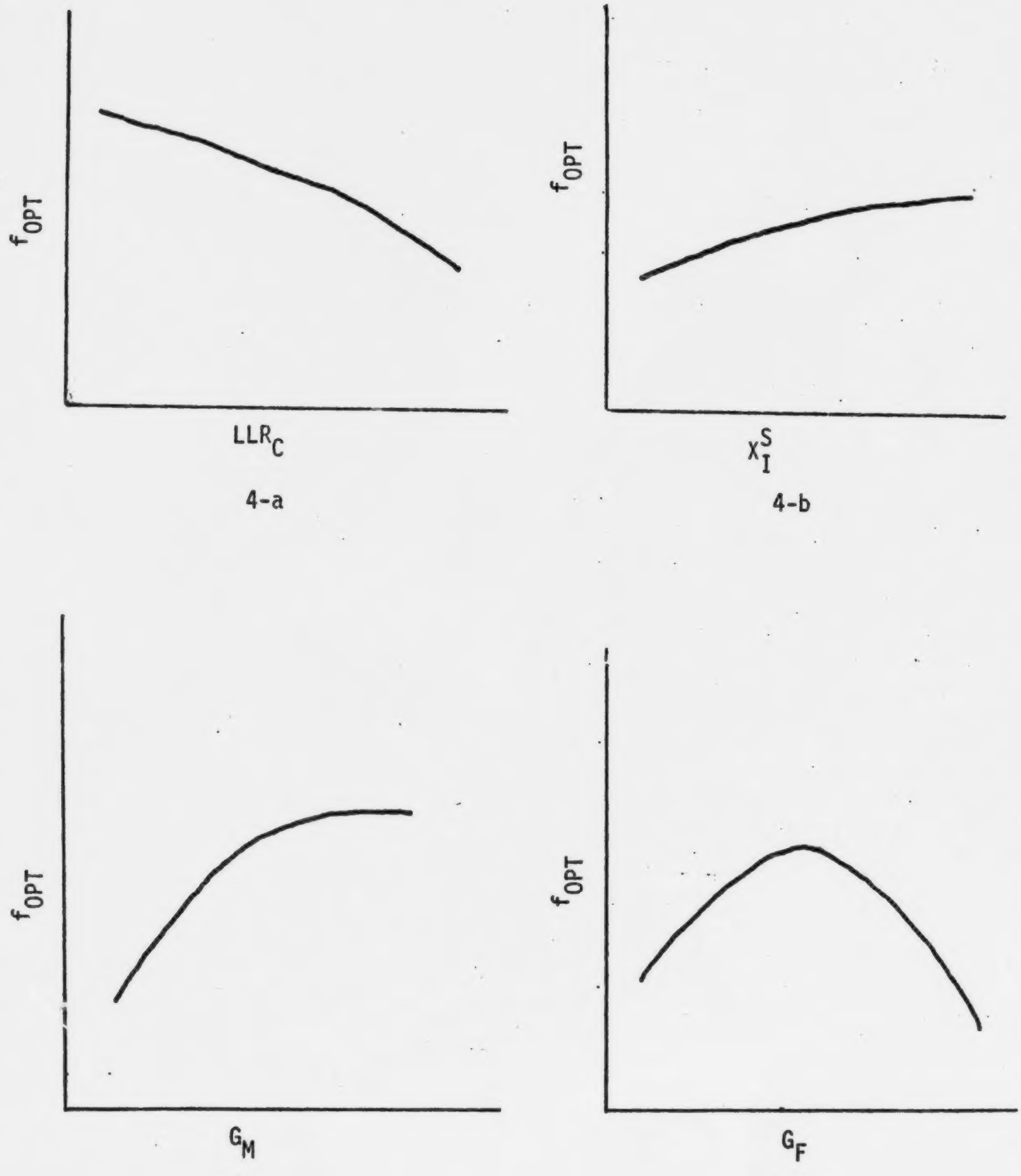
The shapes of the response surfaces defined above in terms of selected variables (and other response surfaces relating to yet additional variables as desired but not discussed herein) can be used to postulate the behavior of the conversion/separation process system in the format of a fundamental set of guidelines for developing a design or an operating program in a functional facility. In either application perspective, the response surface relationships:

- Provide the basis for identifying, in terms of each variable, the boundary conditions and zones of stable performance associated with each variable in a unified framework.

- Permit from the preceding the definition of a region of optimal performance of the conversion/separation processes in terms of ranges of the designated control and chemical dose parameters.

An immediate and evident application of the response surface relationship concept occurs in the operating situations where polymer alone or

PROBABLE SHAPES OF RESPONSE SURFACES



4-a

4-b

4-c

4-d

FIGURE 4

polymer in combination with an inorganic or metal ion coagulant is used in primary separation. For any given level of the control variables LLR_C, X^S, G_M, and G_F (optimized with respect to performance by trial and error) I it is then possible to "map" in parallel laboratory experimental and prototype operating programs the response surface relationship in Figure 3 at two scales, using:

- In one response surface, standard laboratory jar test data.
- In the second response surface, actual chemical dosages to the conversion process and separation process effluent quality data.

By essentially reducing the field operating program to a consideration of the same number of variables as considered in the laboratory jar test program, it can be postulated that the relative shifts in contours between the two equi-dimensional response surfaces relate to scale-up of the process train alone and is not related to any of the control parameters. The operator, having an *a priori* knowledge of the two response surfaces and relative shifts in performance contours due to scale-up, is then in the desirable position of being able to predict at the prototype level the probable impact of increasing or decreasing a chemical dose on a rational basis.

SUMMARY

As a basis for considering the role of polymers as primary coagulants, it is necessary to view the success of the coagulation process as inextricably associated with the performance of the primary separation process following the coagulation and flocculation (or conversion) processes. Within this overall framework for conversion/separation as applied to the water treatment field, polymers represent but one form of chemical additive for effecting or enhancing the conversion step. Unfortunately, the introduction of polymers represents the addition of but one more variable to be considered in conversion/separation at a time when there exists critical gaps between the researcher, the designer, and the operator with respect to sufficient overlap of understanding, such that the experience and knowledge of each can be integrated to improve general, rather than situation-specific, understanding of conversion/separation.

The mechanistic approach to dealing with understanding of conversion/separation processes has dominated all efforts to date towards rationalizing process behavior, but has resulted primarily in the individuals (researchers, designers, operators, and regulatory agencies) pursuing their own particular concepts of conversion/separation and having that concept prevail. Based on the evidence available, the mechanistic approach has resulted in emphasis being placed on the differences in both model and prototype data between different situations rather than on the similarities.

The response surface concept is proposed as an alternative basis to the mechanistic approach for process understanding. This concept offers significant promise as a framework for advancing of the conversion/separation processes in the water treatment field, in that:

- The unit processes can be examined and studied independent of particular applications.

- The conversion/separation process can be dealt with as an entity.
- The relative impact on process train performance of all the design and control variables can be integrated or unified to identify for the designer and operator the ranges of individual process variables in which desired performance and operating characteristics can be obtained.

The use of the response surface concept as a basis for establishing a treatment system design and/or operating objectives is discussed, with particular emphasis on developing operational guidelines for the use of polymers as a chemical pretreatment alternative.

ACKNOWLEDGMENTS

The counsel of Dr. W. E. Gates of Engineering-Science, Inc. in the preparation of this paper is gratefully acknowledged.

REFERENCES

1. "Modern Concepts of Filtration and Their Application to Wastewater Reuse", by W. E. Gates, J. D. Westfield, and T. G. Shea, presented at Second Annual Sanitary Engineering Conference, University of California, Berkeley, June 1970.

2. "Treatment of Dilute Sewages with the Dissolved Air Flotation Process," by R. M. Males and T. G. Shea, Special Publication Series No.11, Engineering-Science, Inc., Cincinnati, Ohio, August 1971.

USE OF POLYELECTROLYTES AS FILTER AIDS

A paper presented June 17, 1971, at the 91st Annual Conference, American Water Works Association, Denver, Colorado, by Robert H. Harris, Director of Technical Services, Turbitrol High Rate Filter Division, The Taulman Company, Atlanta, Georgia.

USE AND CONTROL OF POLYELECTROLYTE FILTER AIDS IN HIGH RATE FILTERS

INTRODUCTION

Since the idea of using filter aids was first conceived by Raymond Pitman about 1958, the use of filter aids to improve the performance of high rate filters has become accepted practice at many water treatment plants throughout the United States. It has been reported that the use of filter aids can result in a substantial savings in primary coagulant[1] and allow filters to be operated at higher rates without danger of turbidity breakthrough.[2] Other researchers have also shown that the use of filter aids will produce a better quality effluent and allow longer filter runs.[3] Of equal importance are the difficulties which have been encountered when some plants have attempted to use a filter aid. Problems with excessive headloss build-up[1] and difficulties with backwashing[4] had been reported. Most of the difficulties can usually be traced to overdoses of filter aid.

In the literature, the terms filter aid and filter conditioner have been used interchangably. In this paper, the author would like to define a filter aid as a chemical continuously added to the influent of a filter which alters the characteristics of the floc so as to improve filter performance. A filter conditioner is a chemical added to the filter only at the beginning of the filter run to condition the media prior to filtration. For instance, the suggestion of Harris[5] to add a polyelectrolyte to the backwash water to improve effluent quality, and the recent work of Burns, Baumann and Oulman[6] with a polymer coated diatomite are examples of the use of filter conditioners.

The low dosage requirements for a filter aid, usually 5-50 ppb, makes accurate feeding difficult and emphasizes the need for a method to determine the exact amount of filter aid required. Most of the methods suggested for determining the proper amount of filter aid have been "Try and See" procedures. Conley and Pitman[2] watched the turbidity of the filter effluent near the end of the filter run. If the effluent turbidity was too high, they would increase the filter aid dosage on the next run. Giese, et al[1] assessed the filter performance at the end of the run, and adjusted the filter aid for the following run. Both these techniques could require several days to determine if the dosage of filter aid used was correct.

This paper will discuss experiences with filter aids in gravity type dual uniform media filters in several water treatment plants in the Southeast. A new and improved method for determining and maintaining the correct dosage of filter aid is described.

FILTER AID MATERIALS

Generally speaking, a filter aid is used to strengthen the floc and make it more filterable. For this reason, most of the chemicals considered good coagulant aids will also make good filter aids. The organic polyelectrolytes have proved to be particularly valuable.

These chemicals are long chains of carbon atoms, colloidal in nature and action. When these polyelectrolytes are dispersed in water, the long ionized chain is kept spread out by the repulsion of like charges distributed along the chain. These charges can be positive (cationic), negative (anionic), or positive and negative (nonionic). Such a large molecule makes an excellent "trap" for colloidal impurities.

When used as a filter aid, the polyelectrolyte bridges between the fine floc particles, which remain after settling. When a "weak floc" condition exists due to undertreatment, or other problems, feeding a polyelectrolyte to the filter influent will entrap the colloidal particles which could possibly pass through the filter and enable them to be removed in the anthracite layer.

Activated silica[7] and ferric sulfate[8] have shown promise as filter aids. Alum is unsatisfactory, as the alum floc forms too slowly and soluble aluminum may pass through the filter bed.

Going back to the definition of a filter aid given in the introduction, a filter aid is a chemical which is continuously added to the influent of the filter which alters the characteristics of the floc so as to improve filter performance. The recent work by Smith and Medlar[9] and others[10] using phosphates to weaken the floc, which resulted in deeper bed penetration, is also another example of a filter aid. The author knows of several plants where the addition of phosphates as a filter aid would probably improve filter performance. In these cases, the floc is much too strong and filtration occurs only in the top few inches of the media bed, resulting in rapid head loss build-up and short filter runs.

The best type of filter aid to use in a particular plant will depend on the nature of floc to be treated. Normally extensive testing is advisable to determine the best filter aid.

A number of filter aid materials were evaluated at the test plants and three nonionic polyelectrolytes were selected for the test work. By coincidence, it turned out that the three polyelectrolytes were all polyacrylamides.

> Nonionic A[*] is described as a synthetic polymer formed by the polymerization of acrylamide. It has a molecular weight of 1,000,000.
>
> Nonionic B[**] is described as a complex synthetic non-ionic polyacrylamide. Molecular weight - unknown.
>
> Nonionic C[***] is described by the manufacturer as a high molecular weight polyacrylamide. Molecular weight 4,000,000.

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[*] Separan NP-10, Dow Chemicals Company
[**] Polyhall M-19, Stein-Hall & Company
[***] Magnifloc 990N, American Cyanamid Company

TECHNIQUES FOR FEEDING FILTER AIDS

A basic set-up for mixing and feeding a filter aid is shown schematically in Figure 1. The equipment shown is designed for use with an organic polyelectrolyte. The use of activated silica requires a more complex system.[7]

It is a general rule in chemistry that the larger the molecule the more difficult it is to put into solution. This is the reason that most polyelectrolytes are difficult to dissolve. The use of a disperser funnel will minimize these difficulties, by insuring that the flakes of polymer are distributed as individual particles in water These dispersed flakes are then easily dissolved, using a minimum of agitation.

The concentration of the filter aid solution, as well as the size of the solution tanks, will vary depending on the size of the treatment plant, dosage of filter aid required, and the capacity of the feed pump. Generally, solutions over 1% are not convenient to use, because of the high viscosity. A diaphragm pump is normally used to meter the filter aid solution. Due to the extremely small amount of liquid being pumped, it is essential to add a considerable amount of dilution water as a carrier.

Rotameters can then be used to split the filter aid solution and apply the proper dosage to each filter influent. Precautions to prevent cross-connections between the dilution water and polymer solution are required. A photograph of this filter aid system is shown in Photo A.

UNIFORM DUAL MEDIA

One feature common to all of the test plants is a uniform dual media high rate filter bed. This bed is composed of an extremely uniform layer of anthracite coal, in which almost 90% of the media is in the size range of 1.0 to 1.4 mm.* This results in an anthracite layer in which the entire 20" depth is useful for floc storage. Sand with an effective size of 0.45 millimeters and a uniformity coefficient under 1.3 was placed beneath the anthracite.* The sand serves to remove colloidal floc which succeeds in passing through the anthracite.

TURBIDITY MONITORING SYSTEM

Another feature which is common to all test plants is a unique turbidity monitoring system*. This system shown schematically in Figure 2, employs sensitive turbidimeters of the 90° scatter nephelometer type. The effluent turbidity from each filter is continuously recorded, to insure that high quality water is being produced. In addition, another sample of water is removed from the filter bed at a point near the interface between the coarse anthracite and fine sand. This sample is also continuously monitored and recorded, using a second turbidimeter. An alternate turbidity monitoring system uses solenoid valves and a selector switch to allow either the interface sample or the effluent sample to flow to a single turbidimeter, as shown schematically in Figure 3. Photo B shows the interface sample screen location at the time of media placement. This device is a specially constructed well screen with slits small enough so that the coal and sand cannot pass through. The interface screen is placed two inches above the fine sand prior to anthracite placement. Photo C shows a turbidimeter stand mounted in the pipe gallery near the filter effluent piping. The best results can be obtained by placing the turbidimeter as close as possible to the filter and allowing the samples to flow by gravity to the turbidimeters. This prevents air bubbles which frequently occur when turbidimeter samples are pumped and also provides for the fastest possible response time.

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* A product of Turbitrol High Rate Filtration Systems

Photo D is the single turbidimeter stand with the sample switching solenoids hidden behind the panel.

The output signal from the turbidimeter is converted into a signal suitable for transmission to a recorder which is located at a point convenient to the operator. In this case (Photo E) it is part of a large central control panel. In Photo F the control module which houses the high turbidity alarm circuitry, as well as switches to select interface or effluent sample, can be seen beneath the recorder. The module can also automatically shut a filter down if the interface or effluent turbidity exceeds a preselected value.

INTERFACE TURBIDITY AND FLOC STRENGTH

The interface turbidity sample is designed as a tool to aid the treatment plant operator in obtaining optimum performance from a dual media filter. A more complete discussion of interface turbidity monitoring may be found in a recent article by the author, published in "Willing Water"[11]. The turbidity value obtained at the interface indicates where floc removal is occurring within the filter bed. For instance, a high interface turbidity indicates that significant amounts of floc are penetrating through the anthracite layer and must be removed by the fine sand. If the sand is forced to carry too much of the load of floc removal, the head loss build-up becomes excessive, or break-through of turbidity could occur into the effluent. It has been shown that to obtain optimum filter performance, 90 to 95% of the turbidity must be removed in the coarse anthracite. When floc removal does not occur in the anthracite layer, the floc is said to be "weak".

The causes of weak floc are almost too numerous to mention. Poor coagulation, insufficient flocculation, high filtration rates, cold water and raw water contaminants, such as phosphates, are just a few of the things which may produce a weak floc. A floc may be sufficiently strong for easy removal in the upper coarse portion of the bed when the filter is operated at 2 GPM/ft.^{2} rate, but this same floc might be described as weak when the filter is at 6 GPM/ft.^{2}. The shear forces resulting indirectly from the higher rate would break up the floc, causing deep bed penetration. The use of filter aids or conditioners to strengthen floc is frequently necessary when filters are operated at rates over 5 GPM/ft.^{2}. At lower rates it is seldom necessary to use an aid, except during periods when "weak" floc occurs.

PLANT TESTING

The technique described in this paper for determining the proper amount of filter aid to use was derived from experience obtained at quite a number of water treatment plants throughout the Unites States, which have uniform dual media and interface turbidity monitoring systems. However, the data in this paper was obtained at three treatment plants in the southeast: Jefferson, Georgia; Spindale, North Carolina; and Riegel Paper Corporation, Riegelwood, North Carolina.

The raw water characteristics and treatment conditions for each of these plants is shown in the table on the following page.

TABLE I

RAW WATER CHARACTERISTICS & TREATMENT CONDITIONS DURING FILTER AID TESTS

	JEFFERSON	SPINDALE	RIEGEL
RAW WATER			
TURBIDITY, J. T. U	16	2	30
COLOR, UNITS	5	0	60
TEMPERATURE, °F	44	33	43
ALKALINITY, TOTAL	18	16	15
CHLORIDE, ppm	10	12	24
HARDNESS, TOTAL	20	16	26
IRON, ppm	0.8	0.1	0.2
pH	7.2	6.6	6.4
SETTLED WATER			
TURBIDITY, J. T. U.	4-7	3-5	7-12
COLOR, UNITS	0	0	10
PLANT TREATMENT			
TYPE	COAGULATION	COAGULATION	COAGULATION
COAGULANT	ALUM	ALUM	ALUM
FLASH MIX	NONE	MECH. AGITATOR	IN-LINE
FLOCCULATION	BAFFLE	REEL	REEL
FLOC. TIME, Min.	10	35	25
SETTLING TIME, Hr.	1	4	2½
FILTER RATE, GPM/Ft.^{2}	5*	2	7-8
FILTER RUNS, Avg.	35	55	27

*6" Dia. Test Filter

The majority of the test data presented in this paper was obtained at the Jefferson, Georgia, water treatment plant. This plant treats about 1 MGD of water from a small creek, using alum. The absence of a flash mix and a simple baffle flocculator produce a floc which is small, weak and poorly formed. To amplify the problem, the settling basins are very short and provide only a theoretical 1½ hours settling time. Filters are operated at 2-3 GPM/ft.^{2}, but filter performance is poor. The effluent turbidity is frequently 0.3 to 0.4 J.T.U. and filter runs seldom exceed 30 hours. This plant has uniform dual media filter beds and interface effluent turbidity monitoring. Unfortunately, this plant does not have the necessary equipment to feed a filter aid on a plant scale. The data for Figures 4 to 10 was collected, using a 6" diameter test filter, shown in Photo G. The filter aid was prepared as a 0.1% solution and fed into the test filter influent, using a peristaltic pump. No dilution water was used. The influent sample for the test filter was the same settled water which was going to the plant filters. The test filter was operated at a constant 5 GPM/ft.^{2} rate during the test work.

The Spindale, North Carolina, treatment plant has conventional alum coagulation-flocculation treatment, with mechanical agitation for the flash-mix reel type flocculators and settling basins with four hours retention time. Filters are operated at flow rates from 2-3 GPM/ft.^{2}. The filters all contain uniform dual media, and during most of the year filter performance is excellent.

However, during the winter months the water temperature drops to just above freezing. This makes coagulation difficult and a "weak" floc results. A filter aid greatly improves the performance of the filters during this period. This plant has interface-effluent turbidity monitoring on each filter. Data for Figure 11 was obtained during an extremely cold period during the winter of 1969. At the time the filter aid was tested, there was about an inch of ice covering the basins.

The Riegel Paper Corp. in Riegelwood, N. C., treats 20 MGD of a colored turbid water. Treatment consists of coagulation with alum and chlorination. Mechanical equipment consists of in-line agitators for mixing chemicals, reel flocculators and settling basins with about 2½ hour retention time. The plant has ten filters, eight rapid sand operated at 3-4 GPM/ft.^{2}, and two uniform dual media filters operated at 7-8 GPM/ft.^{2}. The high-rate filters are equipped with separate interface and effluent turbidimeters and recorders. A filter aid feed system is used to continuously feed filter aid directly onto the filter bed of the two high rate beds.

TEST RESULTS

Data for Figures 4 to 10 were obtained using the 6" test filter at Jefferson, Georgia. Most of the runs were made using a fixed filter aid dosage for the entire run. Total headloss, and also the loss of head for only the sand layer, was recorded every 4 hours. The difference between these two readings shows the headloss which occurred in the course anthracite. Interface and effluent turbidity values were obtained, using one turbidimeter and a cycle timer and solenoid valves which switched samples every 30 minutes. Nonionic C was used for this study.

Figure 4 is a plot of headloss and turbidity when no filter aid was used. Of special note is the interface turbidity which starts to rise after only 4 hours, indicating floc penetration through the anthracite layer. Effluent turbidity slowly increased to 0.35 J.T.U. at the end of the run. The need for a filter aid is apparent due to the early deep bed penetration. Figure 5 is a similar plot, except this time 10 ppb of nonionic C was fed into the filter influent. Some slight improvement was observed in the interface turbidity, indicating slightly more removal in the anthracite. The run was longer (44 hours), but the effluent turbidity continued to climb, as the run progressed.

Figure 6, in which 22 ppb of nonionic C was used, shows a significant improvement in filter performance. The interface turbidity remained low, indicating most of the floc removal was occurring in the top of the bed. The headloss curves also show that most of the headloss was occurring in the anthracite. The effluent turbidity remained under 0.1 J. T. U. throughout the filter run. This would appear to be near the optimum filter aid dose, as almost twice as much water was produced, and the quality was better than when no filter aid was used.

Figure 7 shows the results when 45 ppb of filter aid was used. Although effluent quality was excellent, the interface turbidity and headloss curves show that headloss build-up was excessive in the anthracite layer, resulting in a short filter run.

Figure 8 compares effluent turbidity data from the same 4 filter runs and illustrates the difficulties in using effluent turbidity for control purposes. The near optimum dose (22 ppb) and the overdose (45 ppb) produced identical quality water. The underdose (10 ppb) and the run without filter aid produced water of nearly the same quality throughout parts of the filter runs.

Figure 9 compares total headloss, using different filter aid doses. Very little difference was observed in total headloss when 0, 10, and 22 ppb of filter aid was used. When 45 ppb of nonionic was used, the headloss build-up was excessive. It would be impossible to use headloss as the criterion for determining filter aid dosage.

Figure 10 is a comparative plot of interface turbidity as a function of filter aid dosage. There appears to be a distinct difference between the interface turbidity values obtained when different doses of filter aid were used. These data indicate that the measurement of interface turbidity shows great promise as a method for controlling the addition of filter aids or conditioners. Since the reason for using a filter aid is to strengthen the floc so that it can be removed by the coarse anthracite layer of the filter bed, and the interface turbidity monitoring concept is designed to reveal where floc is being removed within the filter bed, the interrelationship should have been apparent.

In order to test the conclusions drawn from the Jefferson test work, a full scale test run was made at the Spindale Plant. The data is shown in Figure 11. For this test, another nonionic polyelectrolyte, nonionic B, was used. The test procedure was also modified, in that the filter run was allowed to begin without a filter aid. About 17 hours into the run, the interface turbidity had increased to 0.75 J.T.U., indicating substantial floc penetration to the top of the sand. At this point the addition of the filter aid was started at a dosage of 10 ppb. After 4 hours, no change had occurred, and the dosage was increased to 20 ppb. This increase caused an almost immediate decrease in interface turbidity, indicating sufficient polyelectrolyte had been added to cause the floc to be removed in the coarse anthracite media. Subsequent increases to 30 and 40 ppb had little effect except to increase the slope of the headloss curve. Comparison of this run to prior and subsequent plant filter performance substantiated the correctness of the 20 ppb filter aid dose.

Another test run was made at the Riegel Paper Corp. Due to the high filtration rates at this plant, filter conditioner is used continuously. A test run similar to the Spindale test was made, except filter aid addition was begun about 4 hours into the run, and the incremental increases in nonionic polyelectrolyte were made only 30 minutes apart. Photo H shows the actual piece of chart paper from the dual channel strip chart recorder. The breakpoint when the optimum filter aid dosage was obtained is clearly shown in the photograph. The top curve half of the chart paper is interface turbidity, and the bottom half is effluent turbidity.

DISCUSSION

This technique for determining the correct dosage of filter aid has been tried at quite a number of plants with considerable success. This method works with any material which can be successfully used as a filter aid. The filter aid must be started at a known underdose and incrementally increased until the desired floc removal is obtained. If an overdose is applied, it is usually impossible to use the interface concept until the filter has been washed.

It is also frequently desirable to adjust the filter aid dosage during the filter run, beginning with no aid or a small amount, and increasing the dosage as the run progresses.

The cost of using a filter aid will usually vary from 5 to 50 cents per million gallons of water filtered. There is a considerable spread in the price of organic polyelectrolytes, and the dosage requirement can also vary considerably from plant to plant. The average cost of using an organic polyelectrolyte as a filter aid is usually more than offset by the savings in washwater which results.

SUBMERGED ROTARY FILTER AGITATORS

Most of the plants which control filter aids, using this turbidity monitoring concept, have not experienced difficulties with backwash. This may be due in part to the submerged rotary filter agitators* which are placed down in the filter bed near the bottom of the anthracite. These have proved to be more efficient than surface wash agitators, when used in uniform dual media beds, because they aid in removing the floc which has penetrated deep into the anthracite layer.

CONCLUSIONS

A sample of water removed from within a uniform dual media filter bed at a point near the interface between the coarse anthracite and the fine sand, and continuously analysed for turbidity, shows a great promise as a method for obtaining and maintaining the optimum dose of a filter aid or conditioner.

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*A product of Turbitrol High Rate Filter Systems

REFERENCES

1. Giese, G. D., Pitman, R. W. and Wells, G. W. Use of Filter Conditioners in Water Treatment. Jour. AWWA, 59:10 (Oct. 1967).

2. Conley, W. R., and Pitman, R. W. Innovations in Water Clarification. Jour. AWWA, 52:10 (Oct. 1960).

3. Robeck, G. G., Dostal, K. A., and Woodward, R. L. Studies of Modifications in Water Filtration. Jour. AWWA, 56:198 (Feb. 1964).

4. Robeck, G. G. High Rate Filtration Studies, Gaffney, S. C. Water Plant Project Report USPHS, Robt. A. Taft Sanitary Eng. Center, Cincinnati, Ohio (1963).

5. Harris, W. L. High Rate Filter Efficiency. Jour. AWWA, 62:12 (Dec. 1970).

6. Burns, D. E., Bauman, E. R. and Oulman, C. S. Particulate Removal on Coated Filter Media. Jour. AWWA, 62:2 (Feb. 1970).

7. Pitman, R. W., and Wells, G. W. Activated Silica as a Filter Conditioner. Jour. AWWA, 60:10 (Oct. 1968).

8 Dostal, K. A., and Sommerville, G. A., and Robeck, G. G High-Rate and Dual-Media Study in a Northwestern Ohio Water Plant, Project Report USPHS, Robt. A. Taft Sanitary Engr. Center, Cincinnati, Ohio (1966).

9. Smith, C. V. Jr., and Medlar, S. J. Filtration Optimization Utilizing Polyphosphates. Jour. AWWA, 60:8 (Aug. 1968).

10. O'Melia, C. R. and Crapps, D. K. Some Chemical Aspects of Rapid Sand Filtration. Jour. AWWA, 56:10 (Oct. 1964).

11. Harris, R. H. Monitoring and Control of Filtration in Waterworks. Willing Water, 14:15 (Aug. 1970.

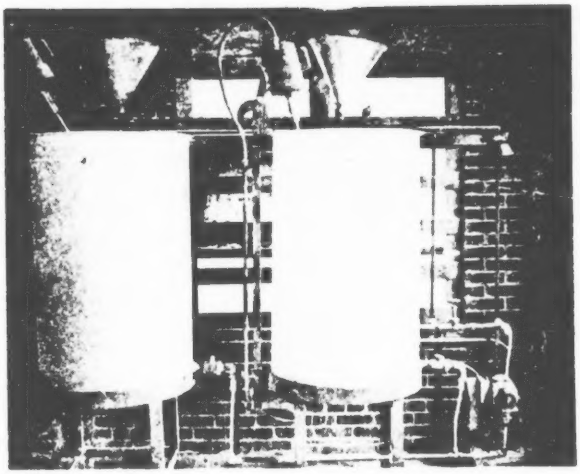

PHOTO A - FILTER AID FEED SYSTEM showing solution tanks, pump, and disperser funnel & agitators.

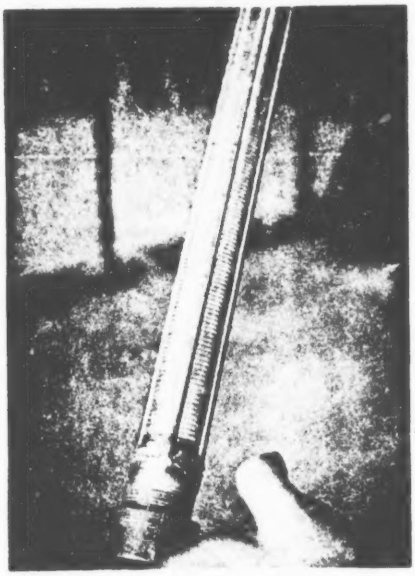

PHOTO B - INTERFACE SAMPLE SCREEN - prior to placement in filter.

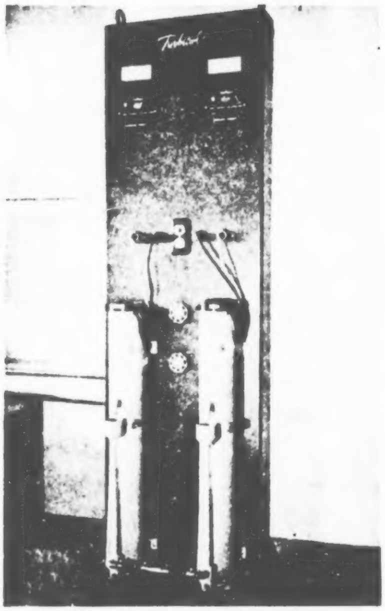

PHOTO C - TURBIDIMETER STAND with separate turbidimeters for interface & effluent turbidity.

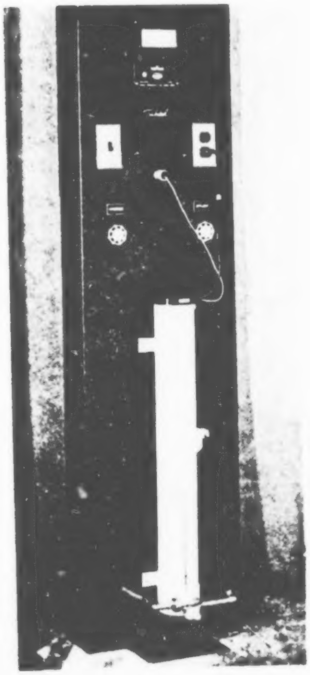

PHOTO D - ALTERNATE TURBIDIMETER STAND with solenoids to select interface or effluent turbidity.

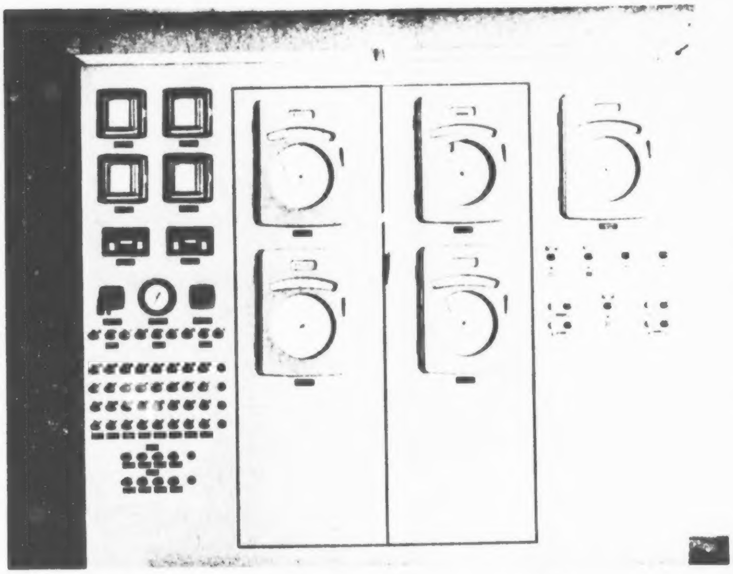

PHOTO E - CENTRAL CONTROL PANEL
with filter turbidity
monitoring system recorders
and control modules at top
left.

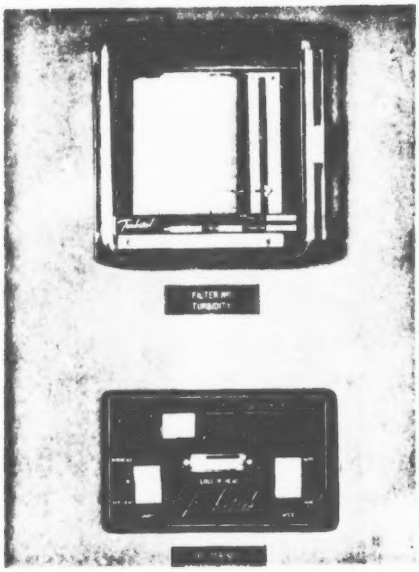

PHOTO F - TURBIDITY RECORDER
AND CONTROL MODULE.

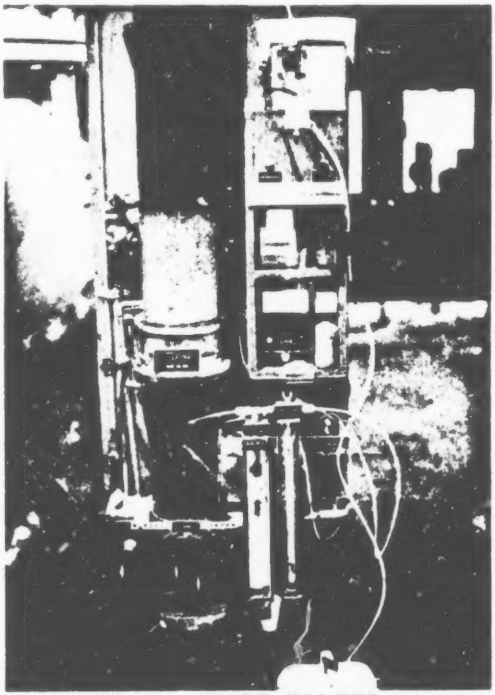

PHOTO G - TEST FILTER
used to obtain
data at Jefferson,
Georgia.

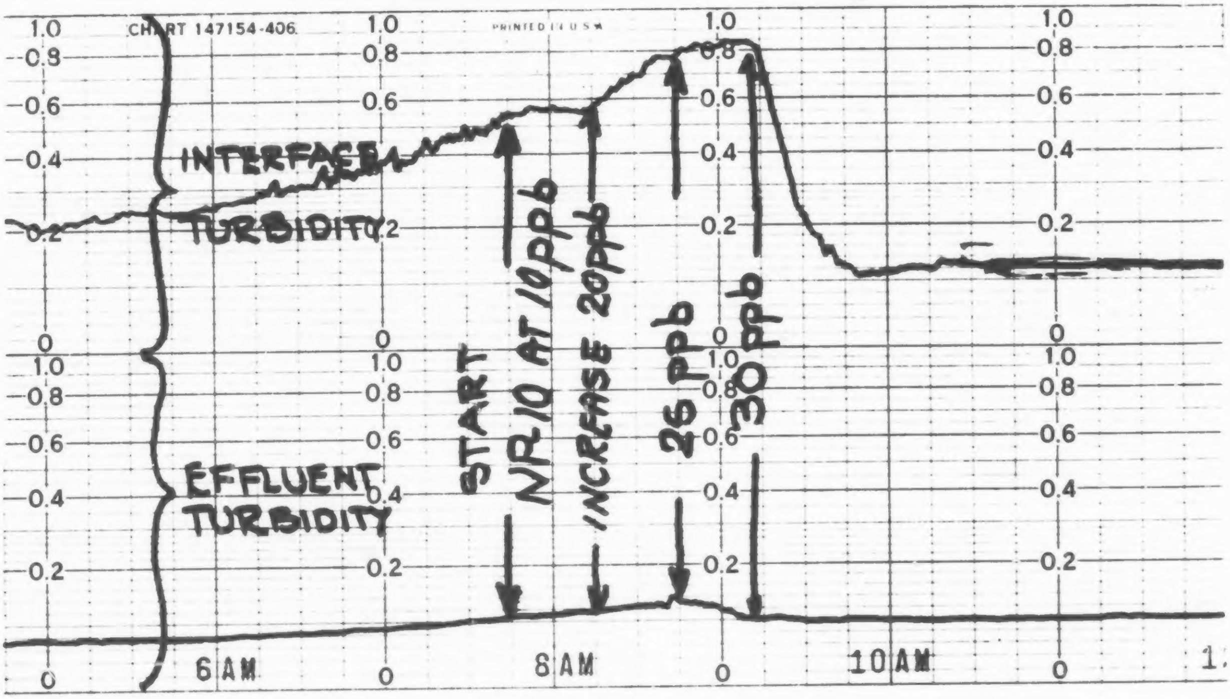

PHOTO H - ACTUAL STRIP CHART FROM RIEGEL PAPER TEST FILTER - showing incremental increases in filter aid until the optimum dosage was reached.

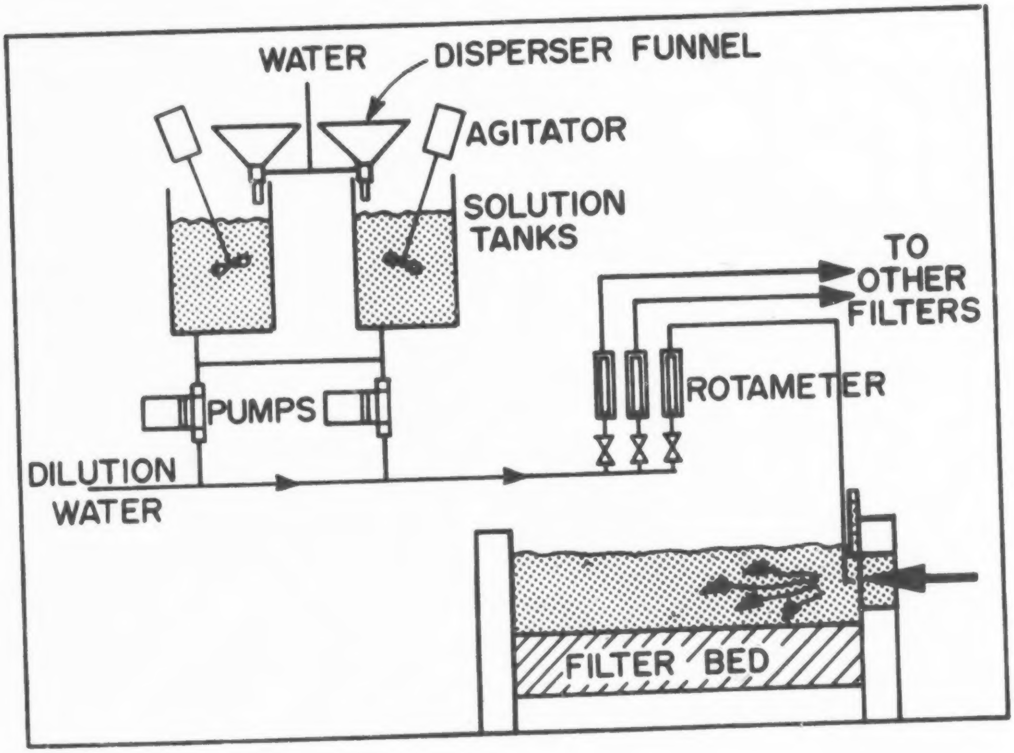
WATER
DISPERSER FUNNEL
AGITATOR
SOLUTION TANKS
TO OTHER FILTERS
PUMPS
ROTAMETER
DILUTION WATER
FILTER BED

FIG. 1 – SCHEMATIC DIAGRAM OF FILTER AID FEED SYSTEM

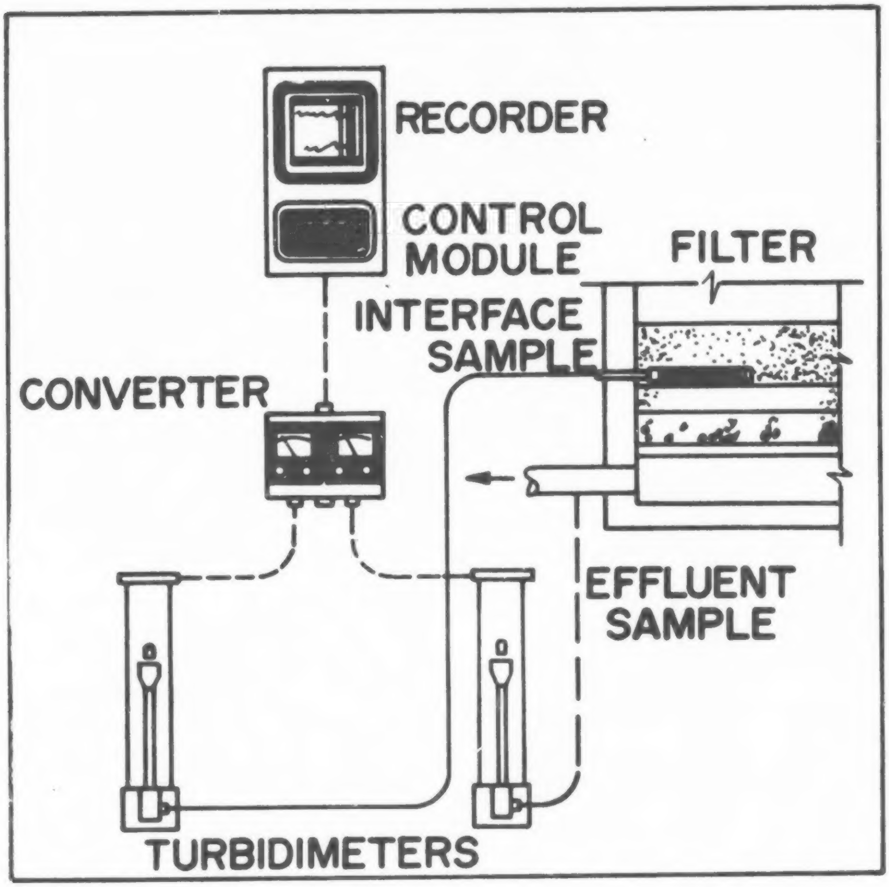
RECORDER
CONTROL MODULE
FILTER
INTERFACE SAMPLE
CONVERTER
EFFLUENT SAMPLE
TURBIDIMETERS

FIG.2 – SCHEMATIC DIAGRAM OF TURBIDITY MONITORING SYSTEM

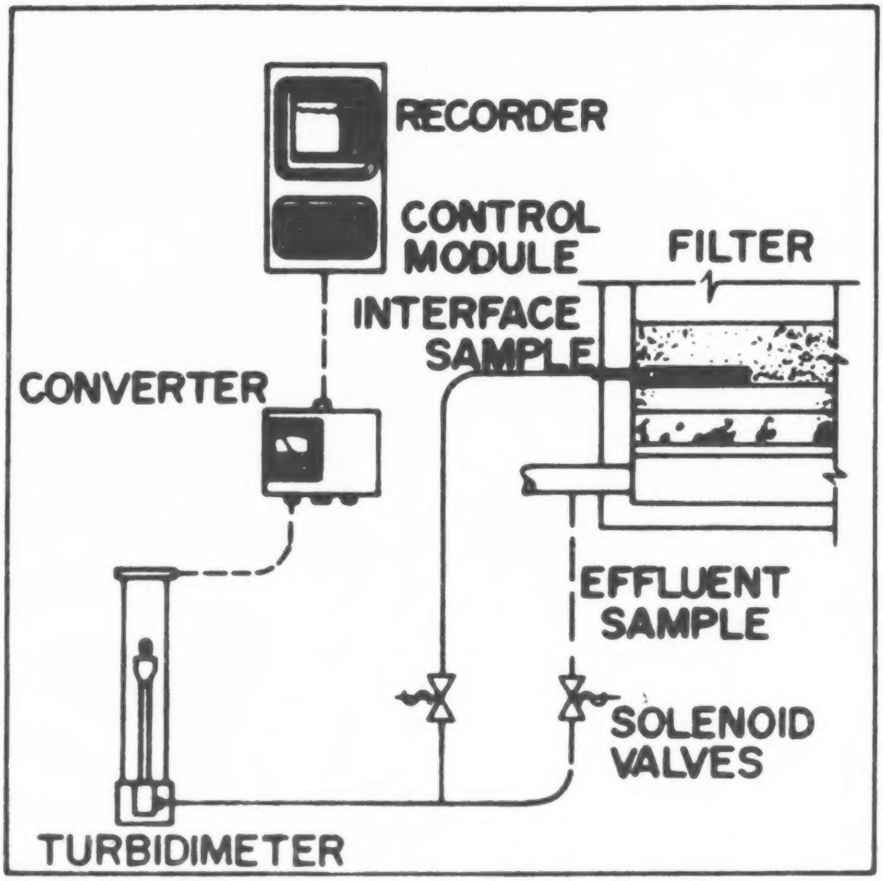
RECORDER
CONTROL MODULE
FILTER
INTERFACE SAMPLE
CONVERTER
EFFLUENT SAMPLE
SOLENOID VALVES
TURBIDIMETER

FIG. 3 – SCHEMATIC DIAGRAM OF ALTERNATE TURBIDITY MONITORING SYSTEM

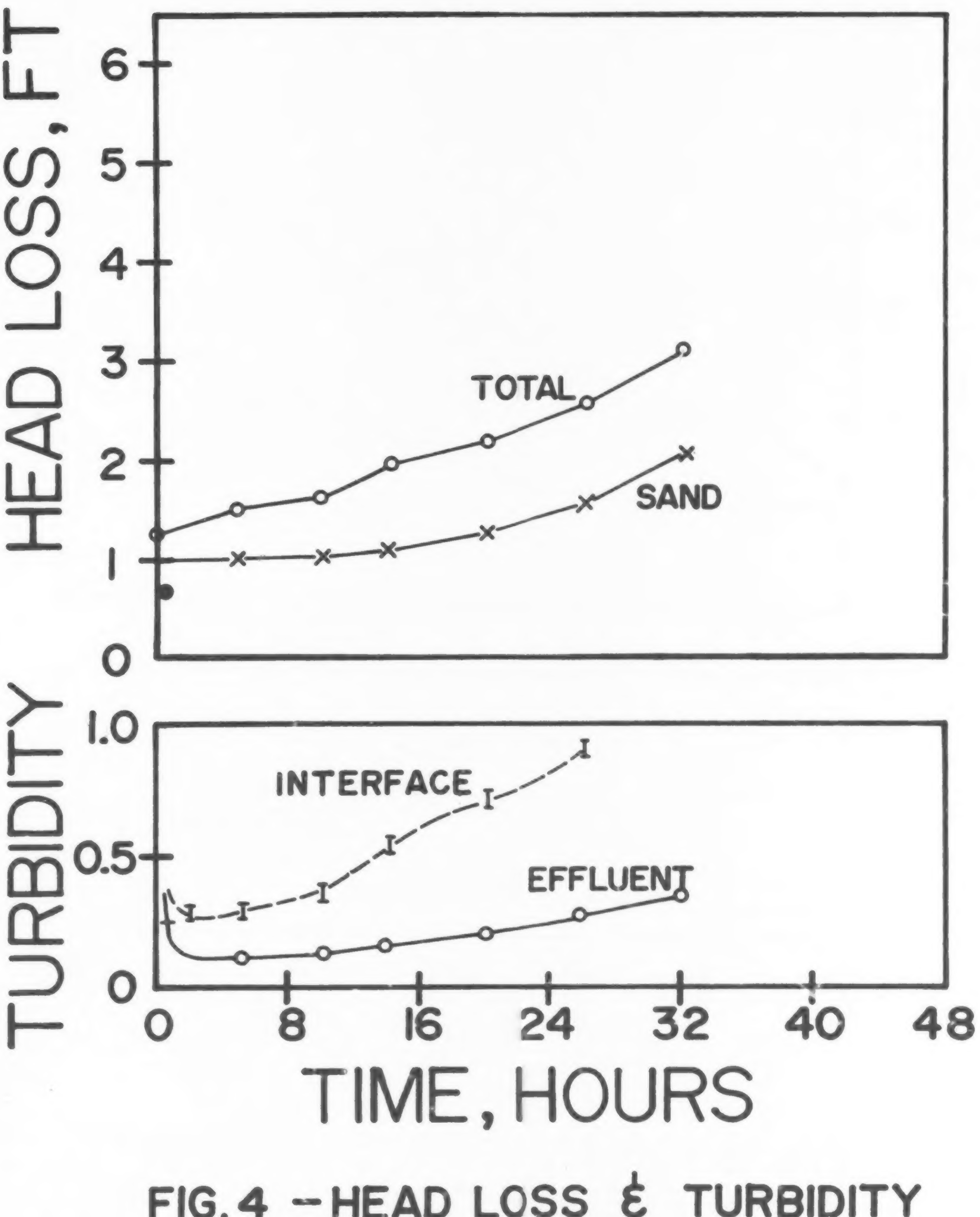

FIG. 4 — HEAD LOSS & TURBIDITY WITHOUT FILTER AID

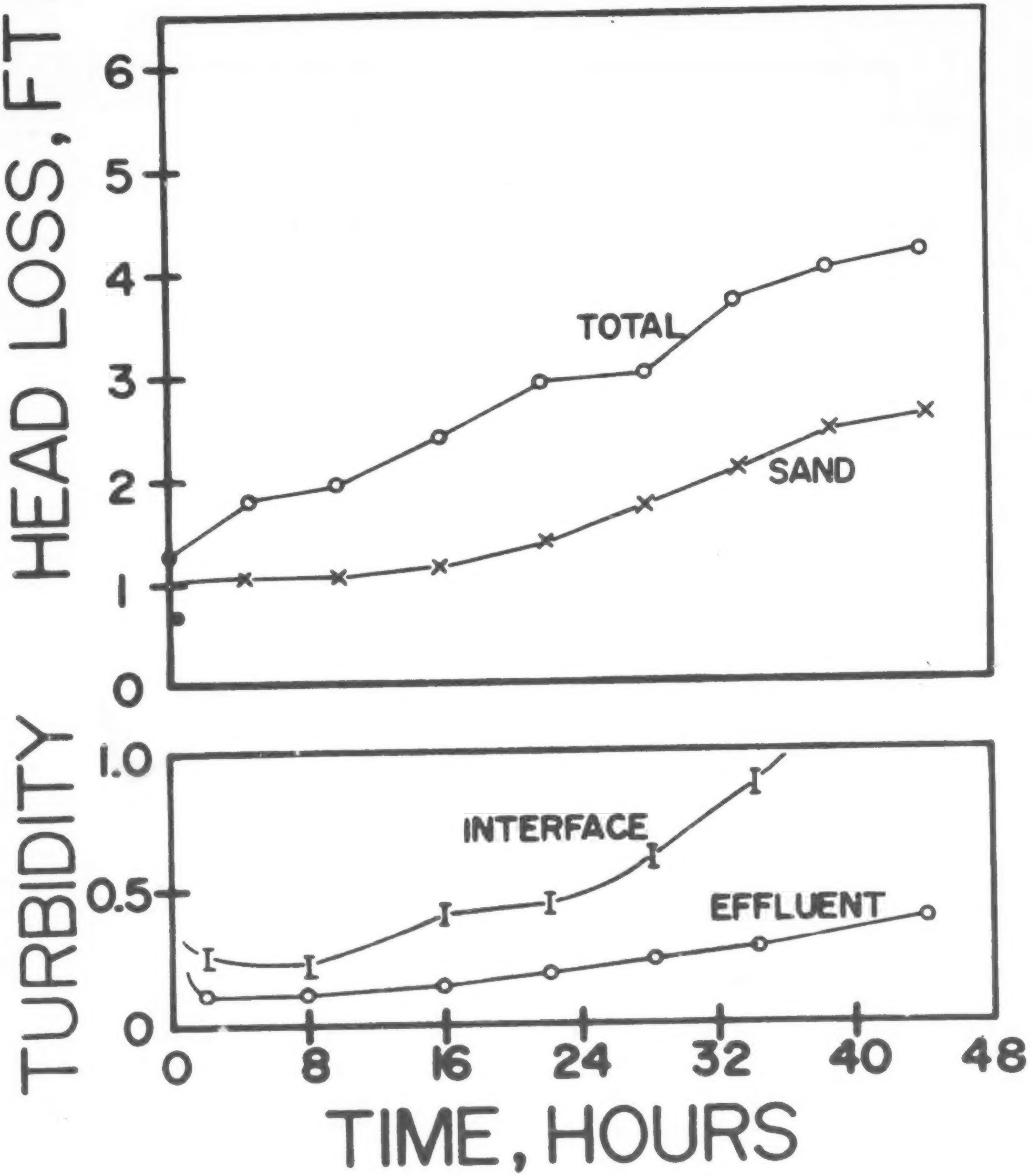

FIG. 5 – HEAD LOSS & TURBIDITY WHEN FEEDING 10 *ppb* NON-IONIC FILTER AID

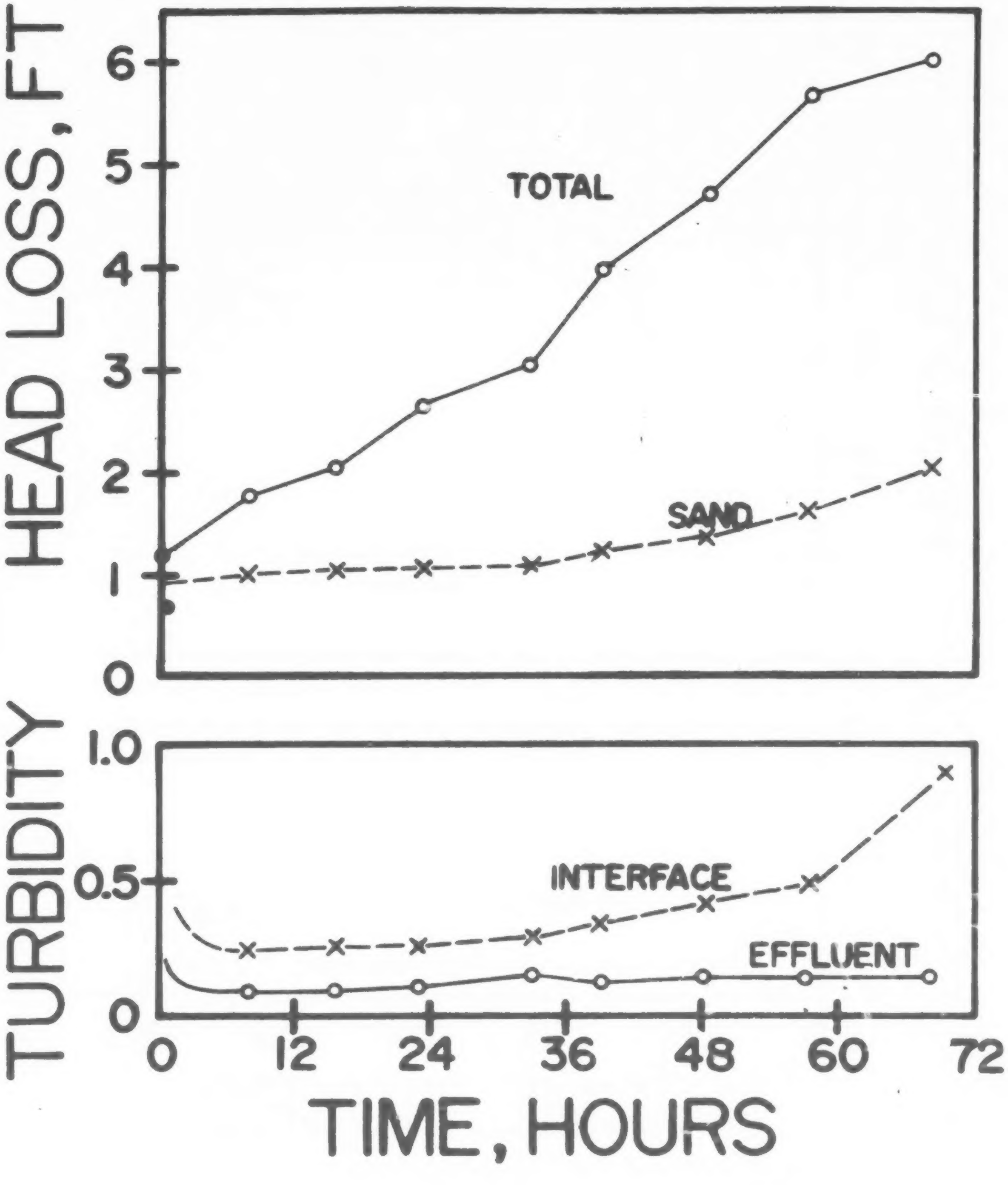

FIG. 6 – HEAD LOSS & TURBIDITY WHEN FEEDING 22 *ppb* NON-IONIC FILTER AID.

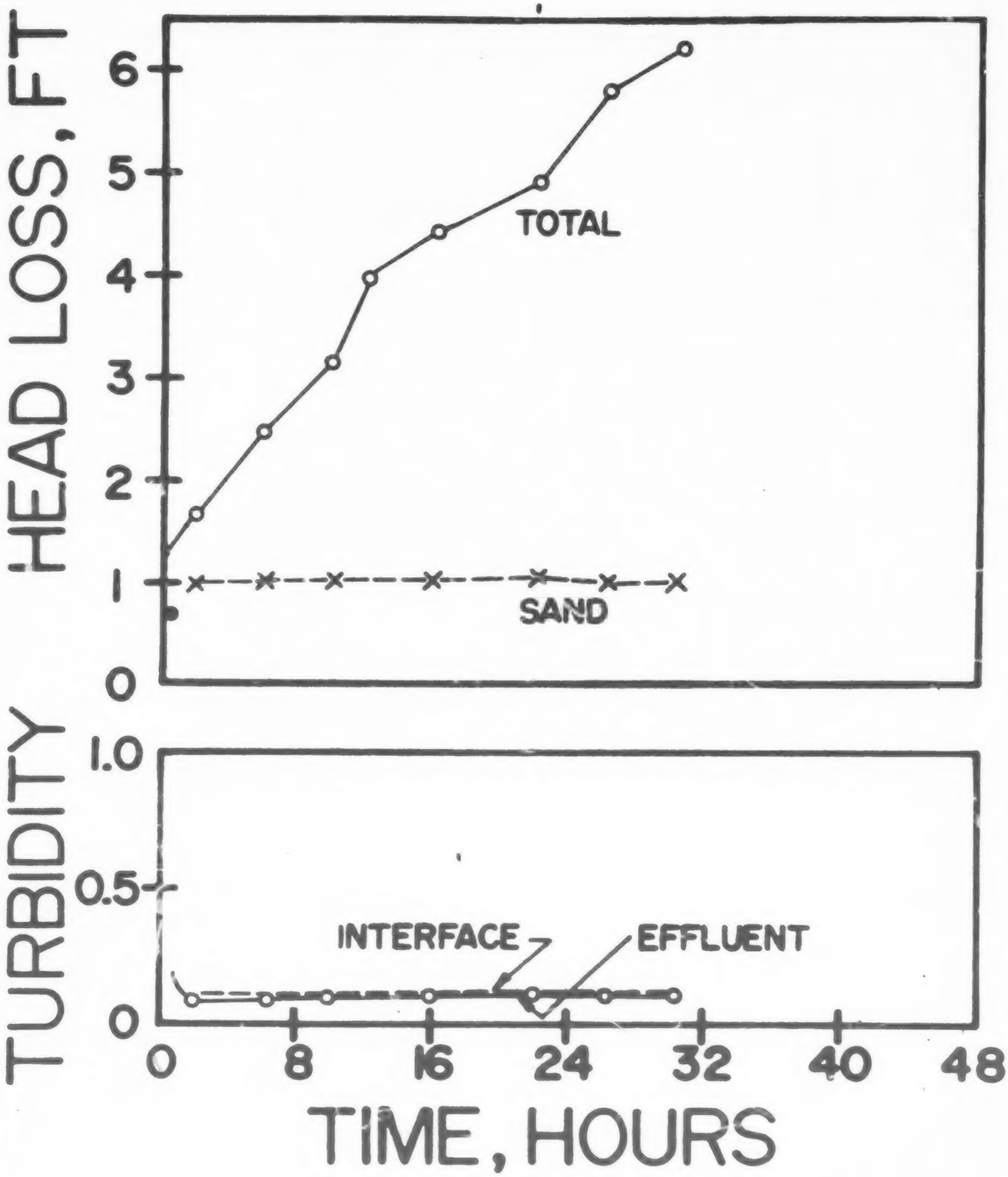

FIG. 7 - HEAD LOSS & TURBIDITY WHEN FEEDING 45 *ppb* NON-IONIC FILTER AID

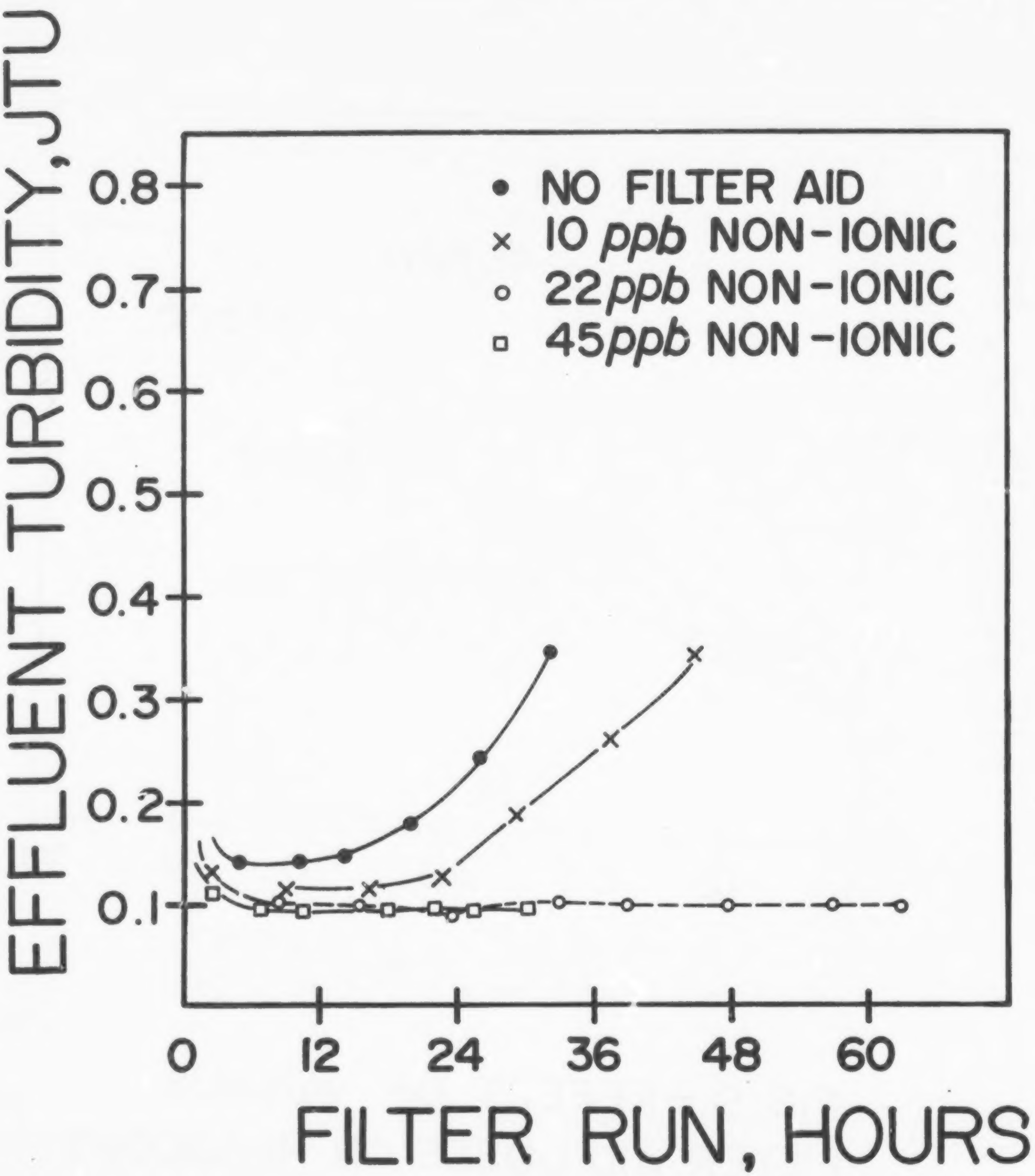

FIG. 8 – EFFECT OF FILTER AID DOSE ON EFFLUENT TURBIDITY

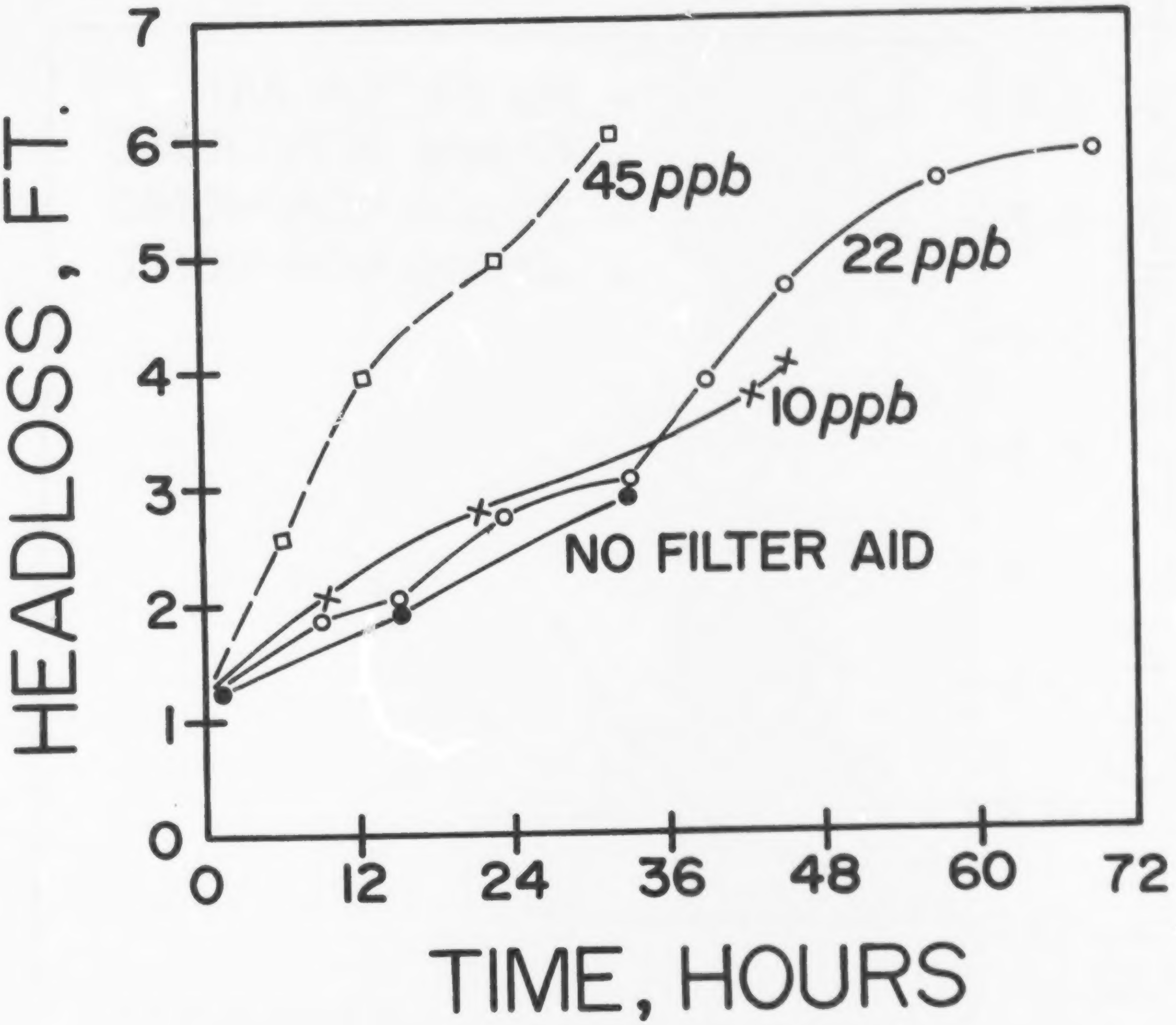

FIG. 9 – EFFECT OF VARIOUS FILTER AID DOSES ON HEADLOSS

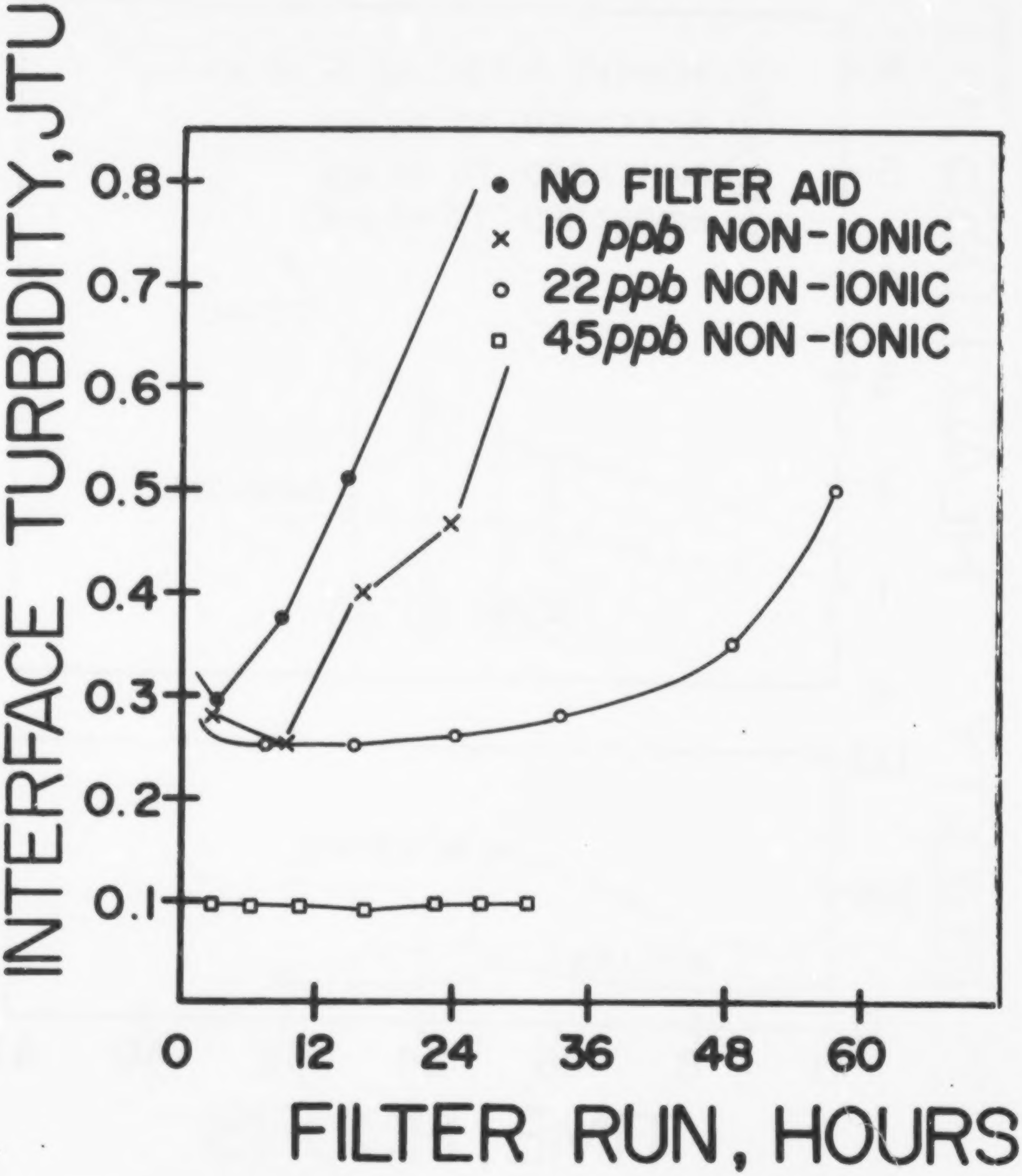

FIG. 10– EFFECT OF FILTER AID DOSE ON INTERFACE TURBIDITY

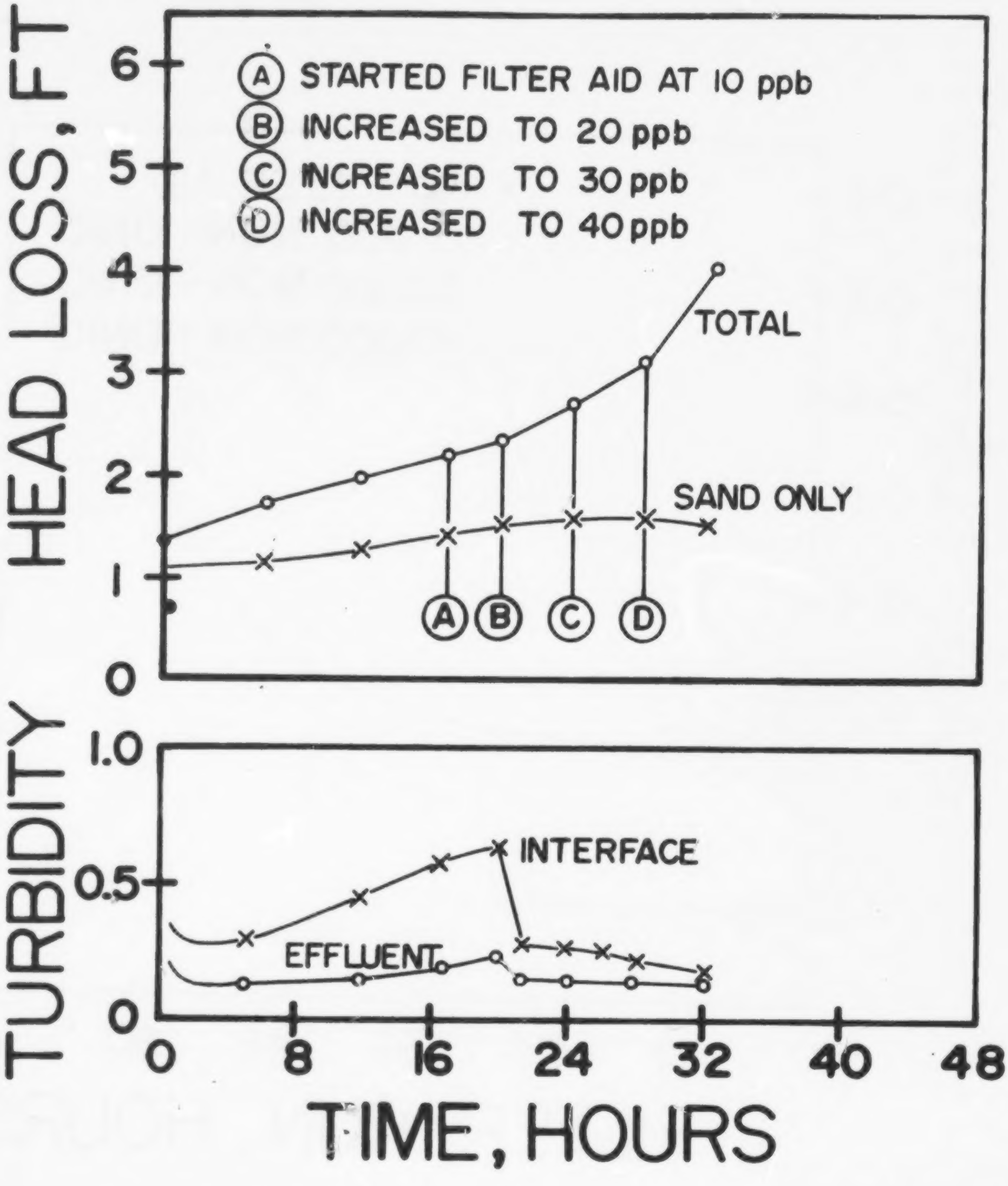

FIG. 11 - USE OF INTERFACE TURBIDITY TO CONTROL FILTER AID AT SPINDALE, N.C

USE OF POLYELECTROLYTES AS AIDS DURING BACKWASH OF FILTERS

W. L. Harris*

For the past four years in California, The Contra Costa County Water District has used a process for adding a small amount of a non-ionic approved polymer as a filter conditioning agent to the backwash water. The arrangement, which makes the addition during a portion of the back flow time, has brought about improved efficiency in rapid sand filter operation and has been duly patented. (U. S. patent 3478880) The improved efficiency has been demonstrated routinely and, as a result, the treatment plant now displays a permit for maximum operation at a 10 gpm/sq. ft. rate. This permit carries with it certain limitations but, in the overall picture, these qualifications are little more than conditions others must expect to meet before gaining similar approval. The path has, therefore, been cleared for maximum plant operation based upon water quality enhancement, without regard to rate. It should be noted that a 10 gpm/sq. ft. rate serves as a common high ground for curbs set by hydraulic factors and need for operating ease, rather than a maximum beyond which a gravity filter process will not produce quality water.

It is fortunate that this improved filter technique developed in a progressive regulatory climate which allowed the achievement of better quality at higher rates to be demonstrated. Management, for its part, was prepared to provide the necessary additional financial outlay without assurance of approval for the new high rate. After more than two years of operation using the technique in the new Ralph D. Bollman water treatment plant, an outstanding consultant in the water treatment field was hired to review and report on the plant's operating capability. His report was based upon both routine and periods of special arrangements to check the plant under more than average arduous conditions. For example, winter conditions with high turbidity values were selected for plant trials at only the maximum rate. Since this rate produced more than the daily demand, it was necessary to have frequent shutdowns and quality water production became more strenuous. The findings in the report had an important part to play in securing the permit. The emphasis is now on quality of plant operation and it is coincidental and entirely unrelated, but worthy of note, that about the time of recognition for very high rate filtration, California made operator certification mandatory.

The need or desirability for conditioning a filter before the start of a run is not new. It was recognized long before the advent of the rapid filter process, as we know it today. Early investigators found that slow sand filters were much more effective in the removal of turbidity after a period of so-called "ripening". This improvement was due to the creation of an adhesive gelatinous build up as a result of of the multiplication of extraneous organisms as the filter run proceeded. The improved condition was regarded as existing in a surface layer, but undoubtedly, the beneficial coating effect extended into the media. The German term "schmutzdecke" for this cover of filth was apparently less offensive in connotation than the English counterpart for describing the state of the filter, and the word remains with us today. When the rapid sand filter process with its much higher rate and attendant coagulation treatment came into vogue, the same basic need for preliminary conditioning of the filter was demonstrated. Removal of a satisfactory amount of influent turbidity in the filter was shown to be dependent upon the use of a coagulant to provide a process distinctly different from that which occurs in straining out heterogeneous particles occurring naturally. This led to arrangements for allowing filters to operate on a filter to waste configuration upon start-up for an indeterminate wasteful period until water of acceptable quality was being produced. This approach to improved water quality has been in the discard for many years at conventional plants and it is totally unacceptable in the concept embraced by high rate to very high rate treatment plant design, namely 5 to 10 gpm/sq. ft. The treatment plant which has furnished the material for this discussion has four filters of an ultimate number of 12, but each filter, when operating at 10 gpm/sq. ft., is at a production rate of 21 million gallons per day. It is not consistent with maximization of plant output to set aside this amount of productive capacity. It should also be noted that automation can move reliably forward only after dependability on quality, maximum rate of output and percentage availability of filter units is known. The 80 mgd capacity plant is not due to be automated, but it is operated by one man per shift and the operator has ample time for the plant's chemical and bacteriological program. Dependability factors are tied to filter condition and it will be immediately recognized that filtering to waste at an insignificant rate provides no assurance of the behavior to expect when the filter is on line. The least uncertainty of quality water production throughout a filter run comes about when filters can be brought on line at maximum rate, if need be, with immediate production of quality water.

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Another approach which is also an apt candidate for discard is the use of a range of values for effluent turbidity that, in turn, provides a canopy to average out high initial start-up turbidity, break-through on surge, or both. The adoption of a range of values may be necessary to cover a wide variety of shortcomings in plant designs, but it is not constructive when used to cover marginal coagulation, operator malaise or official indifference regarding better water quality production.

The use of polymers to condition filter influents for better water quality at higher rates has not changed appreciably since the basic findings by Conley and Pitman(1) were made known. These findings also added pertinent knowledge regarding anthracite sand filters and, in toto, may be considered as having started a new era. Their work was carried out using a non-ionic polymer, but in the ensuing period, a wide variety of anionic, non-ionic and cationic approved polymers have become available. An interesting avenue of thought has brought about studies to perfect filtration-only clarification systems, based upon use of a polymer as the principal coagulant. A study of this nature was commented upon by Kaufman.(2) In the study which used a cationic polymer, it had been shown that only the highest dosage of 1.0 mg/l for a suspension of 6.0 mg/l of clay provided satisfactory removal at a 3 gpm/sq. ft. rate and then only after a prolonged period of ripening. Kaufman comments as follows: "It is somewhat curious that the three polymer dosages (0.5 mg/l, 0.75 mg/l, 1.0 mg/l) display similar ripening characteristics. It is evident that the filter performed poorly until some particle attachment had occurred. Pre-coating the media with the polyelectrolyte would probably have reduced the early period of poor performance." This observation by Kaufman was included in a general discussion of recent theoretical concepts of filtration available for direct filtration of low turbidity raw water. High turbidity waters, especially if from major river systems carrying considerable pollution load, are not likely candidates at this time for short-cutting. But, regardless of handling arrangements prior to filtration, it is universally necessary to condition a filter to arrive at that point in a run where the effluent turbidity value meets the A.W.W.A. goal on quality.

In the Contra Costa County Water District Plant, the polymer added to the backwash is a modified polyacrylamide* of very high molecular weight. The dosage, based upon the total washwater used, is of the order of 0.2 ppm. Since the application covers only a portion of the total wash period, the concentration reaches a maximum approximately three times the average dose. It would be most rewarding, if at this point, the process could be held up for scrutiny and a better understanding of how the benefit is derived. This is a highly desired development which work in the future will probably bring about. Prudence is served by the use of approved polymers in quantities less than allowable limits, but a need which exceeds just curiosity, exists for a more exact knowledge of the mechanisms involved.

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*Magnifloc 985-N, a product of American Cyanamid Company, Wayne, New Jersey.

Filter conditioning is not a substitute or partial replacement for any part of conventional full treatment. The full effect of whatever polymer used is immediate, for there are no means available which offer controlled release and hence sustained action at a level rate. The effect of the conditioning agent must also be tenuous, at best, so that removal of accumulated debris is efficiently accomplished in a normal backwash. The water to be filtered always carries a free chlorine residual of at least 0.5 ppm, so that organic growth on the coated media does not occur.

Acceptable start-up turbidity of the Contra Costa filters has been accompanied by greatly increased resistance to breakthrough due to surge. The demonstration of this ancillary effect was undoubtedly of great help in having burdensome filter rate limits lifted. In a typical demonstration of this improvement, the work is compressed into an 8 hour day. The filter is operated at a 2.5 gpm/sq. ft. rate for 60 to 90 minutes and then successively raised by this amount three times to reach a top rate of 10. Following each successive raise, the filter stays at the newly arrived figure for the same 60 to 90 minutes. When rate changes such as these are performed without breakthrough, it becomes obvious that preliminary conditioning for better filter performance is a valuable adjunct to the water filtration process.

REFERENCES

1 Conely, W. R., and Pitman, R. W. Innovations in Water Clarification, Jour. A. W. W. A., 52; 1319 (Oct. 1960)

2 Kaufman, W. J. Recent Theoretical Concepts of Filtration. Symposium of Water Filtration, May 14, 1969, Bureau of Sanitary Engineering, California State Department of Health, Berkeley, California.

USE OF POLYELECTROLYTES AS A SLUDGE CONDITIONER

Peter W. Doe
Special Projects Manager

June 1972

BACKGROUND OF WATER TREATMENT

Previous speakers will have dealt with other aspects of polyelectrolytes: the theory of their performance, their use, application, and intricacies. Despite this we must begin by putting the matter into perspective in so far as it affects their use in conditioning sludge.

All raw water contains impurities to a greater or lesser extent in both the soluble and insoluble form. If no treatment is given no waste is produced. It follows, therefore, that the greater the quantity of impurities that are removed the greater the quantity of waste that is produced. The purpose of water treatment is to eliminate those substances considered undesirable; taste, odor, hardness, color, suspended solids, bacteria, etc. and the extent to which we remove these together with the nature of the raw water itself, will dictate the type of waste produced. Waste may be of the solid or liquid type. In precipitation treatment we have to use chemicals to assist in the flocculation and coagulation of the suspended solids in the raw water and these chemicals in turn will affect not only the type of sludge but the quantity of the waste product. The characteristics of the raw water is the final factor in determining the characteristics and quantity of the sludge produced.

Before accepting the production and consequent treatment of sludge as inevitable, it must be realized that there are several ways of altering the characteristics of sludge or other waste. To take a simple example, if hard water requires softening, this can be effected by means of an ion exhange softening plant or by chemical precipitation using lime. The first process would produce a liquid effluent which, if near to the sea, could be safely discharged. On the other hand, the second process produces a thick white calcium carbonate sludge which must be disposed of by some means. Selection of the source of water can also reduce or eliminate sludge production. A clean river may need no other treatment than disinfection by chlorine or ozone, whereas a heavily polluted river requires considerable treatment with the inevitable production of large quantities of sludge.

Before we even commence to study the treatment of sludge, the question may well be asked: "Is my sludge production really necessary"?

INFLUENCE OF PRIMARY COAGULANT

Experience over many decades has shown that the most difficult sludge to dewater is an alum sludge, produced by the treatment of raw water with aluminum sulfate resulting in the precipitation of aluminum hydroxide (3). The gelatinous nature of the sludge makes it extremely difficult to dewater, hence a logical line of thought is to consider the replacement of alum as a coagulant by some other chemical. There is a swing at the present moment towards the use of polyelectrolytes as the prime coagulant. Insufficient experience has yet been gained to state positively that this would work with all waters all the time, but there are several instances where alum can be eliminated as the prime coagulant and a suitable polyelectrolyte substituted. The resulting sludge is often far easier to dewater. The prophecy was made in an earlier paper (4) that:

> "the mushroom growth of polyelectrolytes which are at present used mainly as coagulant aids, but which ultimately could possibly be developed as the main coagulant, are going to result in an entirely different type of sludge."

Experience in the years since that statement was made has reinforced the belief that within perhaps as little as ten years the problem of dewatering and disposing of alum sludge will be a thing of the past, at least in newly designed treatment plants. So the use of polyelectrolytes to treat water as opposed to conditioning the sludge may well go part way towards solving the dewatering problem.

COAGULANT AIDS

Some waters when treated with alum produce a very light floc of minimal strength and which are difficult to settle. In such cases a coagulant aid can be used. Heavy minerals can be used to physically weight the floc to assist in settlement. Alternatively, a chemical such as activated silica can be used. The latter, however, is sometimes the prime reason for making the sludge even more difficult to dewater. Polyelectrolytes are now being used as coagulant aids and in consequence have the effect of pretreating the sludge even during the sedimentation stage of water treatment (2). It will thus be seen that polyelectrolytes have three places in water treatment; as a primary coagulant, as a coagulant aid or as a means of conditioning a difficult sludge. Although the purpose of this paper is to discuss their use in conditioning sludge, it is necessary to bear in mind the stage at which polyelectrolytes should be added for maximum benefit to the process as a whole.

USE OF POLYELECTROLYTES WITH SLUDGE

It will be assumed that the primary purpose of the polyelectrolyte will be to condition a thick gelatinous type of sludge for easier disposal. Although the major application will be towards alum sludges, polyelectrolytes can also be used in connection with the sludges formed in the removal of iron from raw water and also in the carbonate type of sludge which results from water softening, or indeed any other type of sludge difficult to dewater.

Polyelectrolytes, or co-polymers as they are often called, are substances of high molecular weight which either occur naturally or are made synthetically. They combine the properties of a water soluble polymer and an electrolyte. The polymer is a high molecular weight material formed by linking up chains of simple molecules, whereas the electrolyte is a chemical substance which dissociates to form ions when dissolved in water. The latter property gives rise to a subdivision of polyelectrolyte, anionic and cationic. There is also a special case of polyelectrolyte which is a long chain of water soluble polymer which is uncharged, and this is termed a non-ionic polyelectrolyte. Many polyelectrolytes are available commercially from a wide variety of manufacturers. They are broadly of two types although each type has the subdivisions referred above. The two types are those derived from naturally occurring materials such as alginates extracted from seaweed or starch products and the synthetic organic polymers. Molecular weights are extremely high compared to conventional molecules. Making the matter even more complicated is the fact the polyelectrolytes are normally produced in two grades; those suitable and approved for use in potable water and those which are toxic and unsuitable for use with potable water.

EFFECT OF POLYELECTROLYTES ON SLUDGE

The thickening of sludge and improvement of the quality of the supernatant is the area in which the greatest benefit can be derived from polyelectrolytes. The effect of the material on a gelatinous sludge is like re-coagulating the sludge, but instead of producing a large number of very fine flocs, it resembles clumps of heavy "fern-like" material up to 1/2" in length. It is actually possible to sieve this material through a stocking or alternatively to pour off the supernatant from a beaker while holding back the floc with the edge of your hand. A crystal clear supernatant usually results. The floc is stronger than before, hence it will stand greater pressure in whatever method of final disposal will be used; for example filer pressing. The difficulty always lies in selecting the right polyelectrolyte to give these very desirable changes, as some polyelectrolytes have not the slightest effect on the sludge in question (5) (7).

The major difficulty with using polyelectrolytes is that with the present state of the theory of polyelectrolytes' action it is not possible to select one scientifically for a specific purpose, and one can only resort to a trial and error method of evaluation. This means a lot of hard labor in the laboratory in trying a multitude of products and selecting the one most suitable for the job in hand.

The decision as to the type of polyelectrolyte to be used is complicated further by the fact that many manufacturers appear most reluctant to give details of the material. As an example of the difficulty in selecting the material, it once took a month to carry out laboratory tests for the use of a polyelectrolyte for a treatment plant, eliminating all except three or four polyelectrolytes from an original list of over 200. In this test it soon transpired that manufacturers tend to market polyelectrolytes which have certain family characteristics. If one polyelectrolyte of such a family did not produce satisfactory results it was reasonably certain that the others would also be unsatisfactory. Similarly if one was successful then the other members of the family would be the same to a greater or lesser extent. A word of warning must be given, however. Raw waters will change due to the seasons of the year, temperature, polluting substances in the water and the like and this may mean that any one polyelectrolyte is not necessarily the optimum choice at all times.

POLYELECTROLYTES AS A SLUDGE CONDITIONER

A sludge can be treated to make it more amenable to dewatering and this process is termed "conditioning".

The effect of polyelectrolytes as a sluge conditioner is two fold. Firstly, it will strengthen the floc and thus the sludge can be concentrated when the supernatant is decanted. Secondly, it can change the physical characteristics of the thickened sludge. These changes can then be utilized in the final treatment and disposal stage. There are several methods for the final treatment and disposal of the sludge:

A. Vacuum filtration.

B. Filter pressing.

C. Freezing and thawing.

D. Lagooning.

E. Disposal into sewers or rivers.

F. Centrifuging and other methods.

It will be seen that the thickening of sludge by conditioning with polyelectrolyte and settling is of great importance to any method of disposal as there is less volume of material to be handled. Bearing in mind that the maximum concentration at which sludge can be handled by pumping is approximately 7%, each method of disposal can be made more efficient and economic by pre-thickening to that percentage.

The addition of a polyelectrolyte prior to centrifuging may also result in a considerable improvement in the centrate, quite apart from the benefit to the sludge itself.

There is one field, however, in which the change in characteristics of the material itself can be exploited to the maximum and this is the filter pressing. It is in this application that polyelectrolytes can have their greatest practical use.

THEORY OF FILTER PRESSING

A filter press is a large mechanical device in which sludge is pumped under pressures as high as 200 lbs. per square inch through filter cloths, the filtrate passing through the cloth which retains the solids while still allowing the filtrate to pass (1). The theory of filtration is attributed to a basic equation derived from the Carman-Kozeny and D'Arcy equations:

$$V^2 = \frac{2P^{1-s} \cdot A^2}{n \cdot r_o \cdot c} \cdot t \qquad \text{--------------------} \ (1)$$

or expressed in terms of the concentration of solids in the final cake:

$$p = c + \left[\frac{2P^{1-s}c\cdot A^2}{r_o \cdot n \cdot v^2}\right]^{\frac{1}{2}} t^{\frac{1}{2}} \quad \text{------------} \quad (2)$$

where:

V = Volume of filtrate

P = Pressure applied on the sludge

s = Compressibility Index

A = Area of filter

t = Time

n = Viscosity of filtrate

r_o = Specific resistance of sludge at unit pressure

c = Initial concentration of solids in sludge

p = Concentration of solids in cake

v = Volume of press

It will be seen that in order to use the equation to predict the performance of a full size press, the coefficient of specific resistance and the compressibility index of the sludge must be known. This can be done in the laboratory and confirmed on a full size press. These two coefficients vary for the type of sludge concerned and will also change depending upon the chemical conditioning. Polyelectrolytes have an influence on these constants. The effect of pressure, the area of filter, time of pressing cycle, etc. are self explanatory. Table 1 below indicates the effect of each variable in equation 2.

TABLE 1

Concentration of solids in the cake
(p) depends on the factors:

	Variable	Symbol	Form	Effect
1.	Time of pressing	t	$t^{\frac{1}{2}}$	Increased time gives disproportionate quantity of filtrate.
2.	Pressure and compressibility index	P] s	$P^{\left(\frac{1-s}{2}\right)}$	When s=o, proportionate to square root, but when s $\rightarrow$ 1, concentration approaches independence of pressure.
3.	Area of Press and Volume of Press	A] v	$\frac{A}{v}$	The smaller the plate thickness the greater the average concentration of the cake in a given time.
4.	Viscosity of Filtrate	n	$\frac{1}{n^{\frac{1}{2}}}$	The lower the viscosity the higher the cake concentration, i.e. better results in warm weather.
5.	Specific resistance at unit pressure	r_o	$\frac{1}{r_o^{\frac{1}{2}}}$	The lower the specific resistance the better.
6.	Initial concentration of sludge.	c	$c+\sqrt{c}$	The greater the initial concentration, the greater the cake concentration.

Considerable work has been done on this subject in England at the Fylde Water Board both by the author and by M. A. Hilson, and some of the results have been published in an excellent paper by M. A. Hilson (6). A full description of the technique used is given in the paper and confirms previous findings that the more important effect of conditioning an alum sludge by polyelectrolytes is the increase in the initial sludge concentration. This is illustrated in Figure 1. Changes in the values of the coefficient of specific resistance and the compressibility index also occur, but in the experiments to date they unfortunately tend to be self-cancelling. Table 2 below illustrates typical figures for various types of sludge.

TABLE 2

Examples	Type of Sludge	Concentration(c)	Compressibility Index(s)	Coefficient of Specific Resistance $(r_o) \times 10^8$
1	Settled backwash water solids from alum treated upland reservoir water with polyelectrolyte as coagulant aid.	1.5%	0.15	62.1
2	As (1) but 1.33mg/gm polyelectrolyte.	1.5%	0.15	17.9
3	As (1) but 2.66mg/gm dry solids polyelectrolyte.	1.5%	0.15	7.5
4	As (1) but using alum alone as coagulant.	0.7%	-0.32	724
5	As (4) but 2.9mg/gm dry solids polyelectrolyte.	0.7%	0.73	0.05
6	Peaty upland water treated on Accentri flocs with alum and polyelectrolyte and 0.35mg/grm polyelectrolyte.	1.43%	0.40	2.9
7	As (6) but 1.05mg/gm polyelectrolyte.	1.43%	0.38	0.44
8	As (6) but 1.40mg/gm polyelectrolyte.	1.43%	0.52	0.14
9	Sludge from river water treated with alum and powdered activated carbon.	5.0%	0.78	5.2
10	As (9) but 15 ppm polyelectrolyte added.	5.0%	0.84	2.1
11	As (9) but without powdered activated carbon.	5.0%	0.64	18.7
12	As (10) but without powdered activated carbon.	5.0%	0.88	1.8

NOTE: Doses expressed as mg/gm are based on dried solids.

It will be seen that any means by which the Compressibility Index and the Coefficient of Specific Resistance can be lowered will increase the volume of filtrate in a given time, i.e. will increase the efficiency of the process. It is unfortunate that no means has yet been reported by which these two factors are improved simultaneously.

Conditioning of sludge to improve filtration can be attempted in various ways. The addition of polyelectrolyte has already been mentioned. Lime and other chemicals such as aluminum chlorohydrate or even inert substances such as fly ash, clay, paper mill waste and powdered chalk have been used. Lime is the most common additive, but quite apart from the obvious rise in pH of the filtrate it has been found experimentally that the BOD of the filtrate will rise alarmingly. A rise in filtrate BOD is also experienced if the sludge is heat treated as a means of conditioning. Polyelectrolytes do not have this effect, hence if the filtrate has to be discharged to a river it will probably meet State Standards without further treatment. This is an important side benefit of using polyelectrolytes as sludge conditioning agents.

There are additional benefits from a practical aspect:

1) The tendency to produce a cake in the press with leathery outside skins and a sloppy center is reduced and a more "handleable" cake is produced in a given time.

2) Cakes tend to strip off the cloths better at the end of the cycle, sometimes eliminating the necessity of precoating.

It must be emphasized that the use of polyelectrolytes to produce a beneficial result on values of the two parameters, compressibility index and coefficient of specific resistance has not yet been proved (8). Any benefit in the one which is not cancelled by a detrimental effect in the other, may well be of less importance than natural changes in raw sludge itself.

SUMMARY

From experience gained using polyelectrolytes in the conditioning of sludge, the following conclusions may be drawn:

1) Polyelectrolytes of high molecular weight may be toxic or non-toxic. Non-toxic polyelectrolytes approved for use with potable water must be used in all water filtration plants where supernatant could intentionally or unintentionally be returned to the head of the plant.
2) Polyelectrolytes of the cationic, non-ionic, or anionic categories may or may not be successful for a given application. Testing in the laboratory or on site must be carried out to determine the efficiency of each polyelectrolyte.
3) Polyelectrolytes come either in powder or liquid form. The skills required to mix powdered polyelectrolytes and the size of dilution tanks required can dictate against their use. Polyelectrolytes in the liquid form are more easily and economically handled.

4) The greatest advantage of polyelectrolytes lies in concentrating the sludge prior to the final method of disposal.

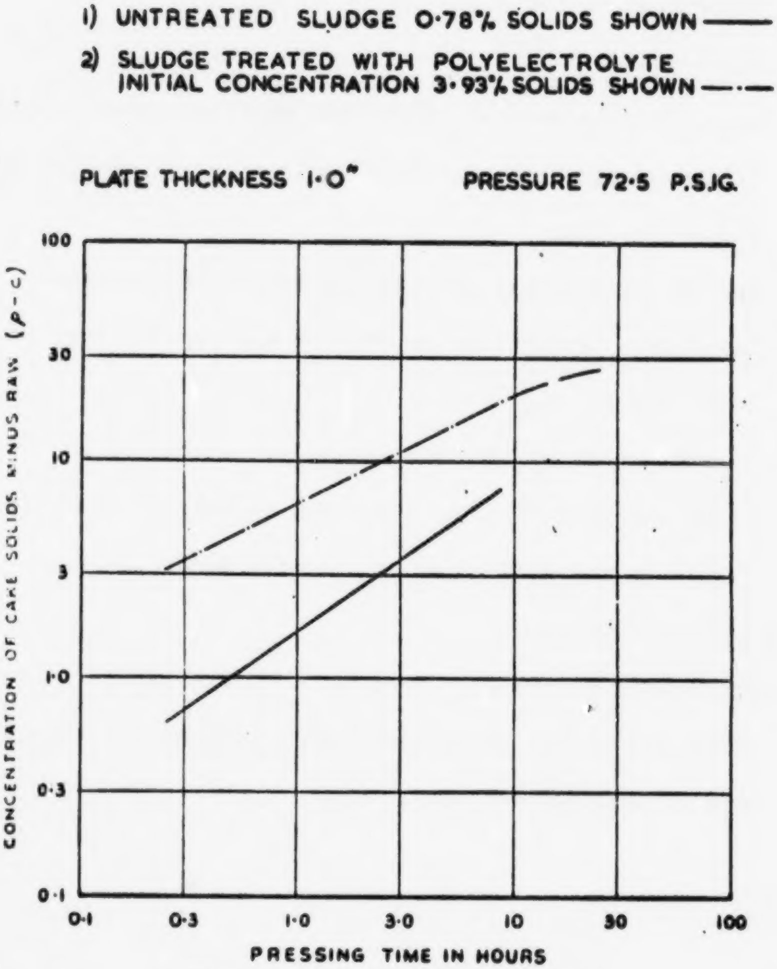
5) Polyelectrolytes also effect the physical characteristics of the sludge, but this is of only marginal benefit in filter pressing.

6) The very low dosage of polyelectrolyte required has normally a large cost benefit in the capital cost of the installation.

7) The effect of adding polyelectrolyte either as a primary coagulant or as a sludge conditioner can often result in the production of a sludge which is more readily dewatered.

8) The use of polyelectrolytes to condition sludge prior to pressing usually leads to a less obnoxious filtrate and a more satisfactory sludge cake.

Fig. 1.



Effect of Pre-thickening Sludge Prior to Pressing

REFERENCES

1 Benn, D. and Bridge, L., "Sludge Disposal by Pressing", Journal, Institution of Water Engineers, Vol. 25, No. 8, 1971.

2 Brown, A. and Leighton, J., "Some Solutions to Sludge Treatment Problems at Fishmoor Treatment Plant", Institution of Public Health Engineers, 1966.

3 Doe, P. W., "The Treatment and Disposal of Washwater Sludge", J.I.W.E., Vol. 12, No. 6, October 1958.

4 Doe, P. W., "A Report on the Disposal of Sludge from Water Treatment Plants, British Waterworks Association, 1968.

5 Gauntlett, R. B., "An assessment of the role of polyelectrolytes in the dewatering of alum clarification sludges with an evaluation of polyelectrolytes of different types", Waterworks Sludge - 3, W.R.A.T.P., No. 46, 1965.

6 Hilson, M. A., "Sludge Conditioning by Polyelectrolytes", Journal, Institution of Water Engineers, Vol. 25, No. 8, 1971.

7 O'Brien and Gere, "Waste Alum Sludge Characteristics and Treatment", Res. Report No. 15 for New York State Department of Health, December 1966.

8 Seddon, F. H., "Thesis on the Disposal of Waterworks Sludge", University of Newcastle-Upon-Tyne, Department of Civil Engineering, October 1968.

SELECTED BIBLIOGRAPHY

The following references have been selected to represent the literature on coagulation and flocculation and does not presume to include all literature citations. Older literature has been cited, even though now thoroughly outdated, to provide a sense of continuity in the historical development of coagulation in water treatment. And finally, the references have been segregated into sections with the full knowledge that many references contain information that can not be restricted to one section alone.

INTRODUCTION AND HISTORY

1. Anon.
Alum: Medium of History
Endeavour, 8, No. 31, 97 (1949).

2. Austen, P.T. and Wilber, F.A.
Report of the Purification of Drinking Water by Alum
Annual Report of the State Geologist of New Jersey, 1884, p. 141,
Trenton, New Jersey (1885).

3. Baker, M.N.
Sketch of History of Water Treatment
JAWWA, 26, 902 (1934).

4. Baker, M.N.
The Quest for Pure Water
Am. Water Works Assoc., New York (1948).

5. Bull, E.V.
Manufacture and Use of Chlorinated Copperas
Proc. of Indiana Water Supply Assn., p. 119 (1912).

6. D'Arcet, F.
Notes Relative to the Clarification of the Water of the Nile and
Water in General which Holds Earthy Substances in Suspension.
(Article from French Journal translated by J. Griscom)
J. Franklin Inst. New Series, 22, 258 (1838).

7. Fair, G.M.
Fifty Years of Progress in Water Purification
JAWWA, 55, 813 (1963).

8. Fuller, G.W.
Water Purification at Louisville
Van Nostrand Publ. Co., New York City (1898).

9. Heberden, W.
Remarks on the Pump-Water of London, and on the Methods of
Procuring the Purest Water.
Medical Trans. College of Physicians (London), 1, 1 (1768).

10. Jeunet, M.C.
Action Clarifiante de Alum sur les Eaux Bourbeuses
Le Moniteur Scientifique Journal (Paris), 7, 1007 (1865).

11. Packham, R.F., Rosaman, D., and Midgley, H.G.
A Mineralogical Examination of Suspended Solids from 9 English Rivers
Clay Mineral. Bull., 4, 239 (1961).

12. Upton, V. and Buswell, A.M.
Titanium Salts as Coagulants
Ind. Eng. Chem., 29, 870 (1937).

13. Wolman, A., Donaldson, W., and Enslow, L.H.
Recent Progress in the Art of Water Treatment
JAWWA, 22, 1161 (1930).

THEORY AND MECHANISM OF COAGULATION

14. Black, A.P.
Theory of Coagulation
Water & Sew. Works, Reference Number (1961). Vol. 108, p. R-192.

15. Black, A.P.
Mechanism of Coagulation in Water Treatment. Discussion
J. San. Eng. Div., Proc. ASCE, 89, #SA1, 75 (1963).

16. Brossett, C., Biedermann, G. and Sillen, L. G.
Studies on the Hydrolysis of Metal Ions, II - the Aluminum Ion, Al^{3+}.
Acta Chem. Scand., 8, 1917 (1954).

17. Ives, K.J.
Mechanism of Coagulation in Water Treatment. Discussion.
J. San. Eng. Div.,Proc., ASCE, 88, #SA6, 117 (1962).

18. Kane, J.C., LaMer, V.K. & Linford, H.B.
Filtration and Electrophoretic Mobility Studies of Flocculated Silica Suspensions
JACS, 86, 3450 (1964).

19. Kruyt, H.R.
Colloid Science - Vols. I and II
Elsevier Publishing Co., New York City (1952).

20. LaMer, V.K.
Coagulation Symposium - Introduction
J. Colloid Sci., 19, 291 (1964).

21. LaMer, V.K. and Healy, T.W.
The Role of Filtration in Investigating Flocculation and Redispersion of Colloidal Dispersions.
J. Phys. Chem., 67, 2417 (1963).

22. Mackrle, S.
Mechanism of Coagulation in Water Treatment
J. San. Eng. Div., Proc., ASCE, #SA3, 1 (1962).

23. Mackrle, S.
Mechanism of Coagulation in Water Treatment - Closure.
J. San. Eng. Div., Proc. ASCE, 89, #SA5, 33 (1963).

24. Matijevic, E.
Detection of Metal Ion Hydrolysis by Coagulation
J. Colloid Sci., 20, 322 (1965).

25. Matijevic, E. and Janauer, G.E.
Coagulation and Reversal of Charge of Lyophobic Colloids by
Hydrolyzed Metal Ions. II. Ferric Nitrate.
J. Colloid and Interface Sci., 21, 197 (1966).

26. Matijevic, E., Mathai, K.G., Ottewill, R.H. and Kerker, M.
Detection of Metal Ion Hydrolysis by Coagulation.III.Aluminum
J. Phys. Chem. 65, 826 (1961).

27. Matijevic E. and Tezak, B.
Detection of Polynuclear Complex Aluminum Ions by Means of Coagulation
Measurements
J. Phys. Chem., 57, 951 (1953).

28. Mattson, S.
Cataphoresis and the Electrical Neutralization of Colloid Material
J. Phys. Chem., 32, 1532 (1928).

29. Morgan, J.J. and Stumm, W.
Mechanism of Coagulation in Water Treatment. Discussion
J. San. Eng. Div., Proc. ASCE, 88, #SA6, 119 (1962).

30. Mysels, K.J.
Introduction to Colloid Chemistry
Interscience Publishing Co., New York City (1959).

31. Overbeek, J.Th.G.
Advances in Colloid Science, Vol. III
Interscience Publishing Co., New York City (1950).

32. Packham, R.F.
The Theory of the Coagulation Process - A Survey of the Literature. I.
The Stability of Colloids
Proc. Soc. Wat. Treatment and Examination, 11, 50 (1962).

33. Packham, R.F.
Mechanism ofCoagulation in Water Treatment. Discussion.
J. San. Eng. Div., Proc. ASCE, 88, #SA6, 121 (1962).

34. Pokras, L.
On the Species Present in Aqueous Solutions of "Salts" of Polyvalent Metals
J. Chem. Ed., 33, 152 (1956).

35. Priesing, C.P.
A Theory of Coagulation Useful for Design
Ind. Eng. Chem., 54, 38 (1962).

36. van Olphen, H.
Internal Mutual Flocculation in Clay Suspensions
J. Colloid Sci., 19, 313 (1964).

37. Verwey, E.J.W. and Overbeek, J.Th.G.
Theory of the Stability of Lyophobic Colloids
Elsevier Publishing Co., Amsterdam (1948).

COAGULATION IN WATER TREATMENT

38. Anon.
What Concentration of Aluminum is Normal Following Coagulation and Filtration?
Proc. Soc. Wat. Treatment and Examination, 3, Part 2, 89 (1954).

39. Black, A.P.
The Chemistry of Water Treatment
Wat. and Sew. Wks., 95, 142 (1948).

40. Black, A.P.
Basic Mechanisms of Coagulation
JAWWA, 52, 492 (1960).

41. Buswell, A.M. and Edwards, G.P.
Some Facts About Residual Alum in Filtered Water
Chem. and Metall. Engng., 26, 826 (1922).

42. Gager, K.H., Thompson, L.C., and Zajieck, O.T.
The Solubility of Aluminum Hydroxide in Acidic and Basic Media
Can. Jour. Chem., 36, 1268 (1958).

43. Haney, P.D.
Principles of Flocculation Related to Water Treatment
Proc. ASCE, J. Hydraulic Div., 82, No. HY4, 1036 (1956).

44. Hopkins, E.S.
Composition of Alum Floc in Mixing Basin
JAWWA, 12, 405 (1924).

45. Hudson, H.E., Jr.
Physical Aspects of Flocculation
JAWWA, 57, 885 (1965).

46. Kellogg, J.W.
Residual Alum in North Carolina Filtered Waters
JAWWA, 23, 92 (1931).

47. Kemmer, F.N. and Odland, K.
Demineralizer Performance and the Coagulation Process
Wtr. Works and Wastes Eng., 2, #10, 44 (1965).

48. Langelier, W.F. and Ludwig, H.F.
Mechanism of Flocculation in the Clarification of Turbid Waters
JAWWA, 41, 163 (1949).

49. Langelier, W.F. and Ludwig, H.F.
Flocculation Phenomena in Turbid Water Clarification
Proc. ASCE, 78, No. 118 (1952).

50. Langelier, W.F., Ludwig, H.F., and Ludwig, R.G.
Flocculation in the Clarification of Turbid Waters
Trans. ASCE, 118, 147 (1953).

51. Miller, L.B.
On the Composition of the Precipitate from Partially Alkalinized Alum Solutions
Publ. Health Reports, 38, 1995 (1923).

52. Miller, L.B.
Adsorption of Aluminum Hydrate Considered as a Solid Solution Phenomenon
Publ. Health Reports, 39, 1502 (1924).

53. Miller, L.B.
Some Properties of Iron Compounds and Their Relation to Water Clarification
Publ. Health Reports, 40, 1413 (1925).

54. Packham, R.F.
The Theory of the Coagulation Process - A Survey of the Literature.
II. Coagulation as a Water Treatment Process.
Proc. Soc. Wtr. Treat. & Exam., 11, 106 (1962).

55. Packham, R.F.
Some Studies of the Coagulation of Dispersed Clays with Hydrolyzing Salts
J. Colloid Sci., 20, 81 (1965).

56. Stumm, W. and Morgan, J.J.
Chemical Aspects of Coagulation
JAWWA, 54, 971 (1962).

57. Symons, G.E.
Water Works Practices; Coagulation
Water and Sewage Wks., 102, 470 (1955).

58. Trelles, R.A., Bengolea, D.J., and Poccard, A.G.
Fractionated Coagulation - A New Procedure
JAWWA, 32, 742 (1940).

59. Wolman, A. and Hannan, F.
Residual Aluminum Compounds in Water Filter Effluents
Chem. and Metall. Engng., 24, 728 (1921).

FACTORS INFLUENCING COAGULATION

60. Armstrong, K.C.
Effect of Turbidity on Coagulant Dosage
Water Works, 66, 495 (1927).

61. Bartow, E., Black, A.P., Sansbury, W.E.
Formation of Floc by Ferric Coagulants
Ind. Eng. Chem., 25, 398 (1933).

62. Bartow, E. and Peterson, B.F.
Effect of Salts on the Rate of Coagulation and the Optimum Precipitation of Alum Floc
Ind. Eng. Chem., 20, 51 (1928).

63. Baylis, J.R.
The Use of Acids with Alum in Water Purification and the Importance of Hydrogen-Ion Concentration
JAWWA, 10, 365 (1923).

64. Baylis, J.R.
Factors Influencing the Toughness of Coagulated Matter
Water Wks. and Sewerage, 77, 184 (1930).

65. Baylis, J.R.
Coagulation, Part 4, Effect of the Concentration of Alkaline Carbonates and Neutral Salts
Waterwks and Sewerage, 84, 426 (1937).

66. Black, A.P.
Coagulation with Iron Compounds
JAWWA, 26, 1713 (1934).

67. Black, A.P. and Chen, C.
Electrophoretic Studies of Coagulation and Flocculation of River Sediment Suspensions with Aluminum Sulfate
JAWWA, 57, 354 (1965).

68. Black, A.P. and Christman, R.F.
Electrophoretic Studies of Sludge Particles Produced in Lime-Soda Softening
JAWWA, 53, 737 (1961).

69. Black, A.P. and Hannah, S.A.
Electrophoretic Studies of Turbidity Removal by Coagulation with Aluminum Sulfate
JAWWA, 53, 438 (1961).

70. Black, A.P., Rice, O. and Bartow, E.
Formation of Floc by Aluminum Sulfate
Ind. Eng. Chem., 25, 811 (1933).

71. Black, A.P. and Walters, J.V.
Electrophoretic Studies of Turbidity Removal with Ferric Sulfate
JAWWA, 56, 99 (1964).

72. Buswell, A.M. and Greenfield, R.E.
Investigation by Means of the Hydrogen Electrode of the Chemical Reactions Involved in Water Purification
J. Amer.Chem. Soc., 44, 1435 (1922).

73. Camp, T.R., Root, D.A. and Bhoota, B.V.
Effects of Temperature on Rate of Floc Formation
JAWWA, 32, 1913 (1940).

74. Catlett, G.F.
Optimum Hydrogen Ion Concentrations for Coagulation of Various Waters
JAWWA, 11, 887 (1924).

75. Cohen, J.M., Rourke, G.A., and Woodward, R.L.
Ferric Sulfate Coagulation in the Presence of Synthetic Detergents
JAWWA, 51, 1255 (1959).

76. Cross, J.T., Gallaher, W.U., Filicky, J.G., and Hassler, J.W.
Effects of Synthetic Detergent Pollution
JAWWA, 42, 17 (1950).

77. Hatfield, J.
Hydrogen-Ion Concentration and Soluble Aluminum in Filter Plant Effluents
JAWWA, 11, 554 (1924).

78. Hopkins, E.S.
Composition and Use of Ferric Hydroxide as a Coagulant
Ind. Eng. Chem., 21, 58 (1929).

79. Howells, D.H. and Sawyer, C.N.
Effect of Synthetic Detergents on Chemical Coagulation of Water
Wtr. & Sew. Works, 103, 71 (1956).

80. Kim, W., Ludwig, H.F., and Bishop, W.D.
Cation-Exchange Capacity and pH in the Coagulation Process
JAWWA, 57, 327 (1965).

81. Langelier, W.F.
Coagulation of Water with Alum by Prolonged Agitation
Eng. News-Record, 86, 924 (1921).

82. Marion, S.P. and Thomas, A.W.
Effect of Diverse Anions on the pH of Maximum Precipitation of "Aluminum Hydroxides"
J. Colloid Sci., 1, 221 (1946).

83. Mattson, S.J.
Cataphoresis and the Electrical Neutralization of Colloidal Material
J. Phys. Chem., 32, 1532 (1928).

84. Miller, L.B.
A Study of the Effects of Anions Upon the Properties of "Alum Floc"
Publ. Health Reports, 40, 351 (1925).

85. Morgan, J.J. and Engelbrecht, R.S.
Effects of Phosphates on Coagulation and Sedimentation of Turbid Waters
JAWWA, 52, 1303 (1960).

86. O'Melia, C.R. and Stumm, W.
Aggregation of Silica Dispersions by Iron (III)
Preprints of Papers Presented at 150th Natl. Meeting ACS, Div. Water, Air, & Waste Chemistry, Vol. 5, #2, 86 (1965).

87. Packham, R.F.
The Coagulation Process. Part 1. Effect of pH and the Nature of Turbidity
J. Appl. Chem., 12, 556 (1962).

88. Packham, R.F.
The Coagulation Process. Part 2. Effect of pH on the Precipitation of Aluminum Hydroxide
J. Appl. Chem., 12, 564 (1962).

89. Packham, R.F.
The Coagulation Process. A Review of Some Recent Investigations
Proc. Soc. Water. Treat. and Exam., 12, 15 (1963).

90. Peterson, B. and Bartow, E.
Effect of Salts on the Rate of Coagulation and the Optimum
Precipitation of Alum Floc
Ind. Eng. Chem., 20, 51 (1928).

91. Pilipovich, J.B., Black, A.P., Eidsness, F.A., and Stearns, T.W.
Electrophoretic Studies of Water Coagulation
JAWWA, 50, 1467 (1958).

92. Sedlander, N.R. and Gates, C.D.
Effect of Alkylbenzenesulfonate on Hydrous Alumina Floc
Ind. Eng. Chem., Process Design Develop., 4:1:55 (1965).

93. Smith, O.M.
The Removal of Clay and Silica from Water
JAWWA, 7, 302 (1920).

94. Smith, R.S., Cohen, J.M. and Walton, G.
Effects of Synthetic Detergents on Water Coagulation
JAWWA, 48, 55 (1956).

95. Theriault, E.J. and Clark, W.M.
An Experimental Study of the Relation of Hydrogen-Ion Concentrations
to the Formation of Floc in the Alum Solutions
Publ. Health Reports, 38, 181 (1923).

96. Vaughn, J.C., Falkenthal, R.F., and Schmidt, R.W.
Effects of Synthetic Detergents on Water Treatment
JAWWA, 48, 30 (1956).

97. Velz, C.J.
Influence of Temperature on Coagulation
Civil Eng., 4, 345 (1934).

98. Weiser, H.B., Milligan, W.O., and Purcell, W.R.
Alumina Floc. X-Ray Diffraction Study
Ind. Eng. Chem., 32, 1487 (1940).

COAGULATION OF COLOR

99. Black, A.P. and Christman, R.F.
Characteristics of Colored Surface Waters
JAWWA, 55, 753 (1963).

100. Black, A.P. and Christman, R.F.
Chemical Characteristics of Fulvic Acids
JAWWA, 55, 897 (1963).

101. Black, A.P., Singley, J.E., Whittle, G.P. and Maulding, J.S.
Stoichoimetry of the Coagulation of Color-Causing Organic Compounds with Ferric Sulfate
JAWWA, 55, 1347 (1963).

102. Black, A.P. and Willems, D.G.
Electrophoretic Studies of Coagulation for Removal of Organic Color
JAWWA, 53, 589 (1961).

103. Enslow, L.H.
Chlorinated Copperas and Ferric Chloride as Coagulants
Munic. News and Water Works, 76, 227 (1929).

104. Hall, E. S. and Packham, R.F.
Coagulation of Organic Color with Hydrolyzing Coagulants
JAWWA, 57, 1149 (1965).

105. Miller, L.B.
Notes on the Clarification of Colored Water
Publ. Health Reports, 40, 1472 (1925).

106. Packham, R.F.
Studies of Organic Color in Natural Water
Proc. Soc. Water Treat. and Exam., 13, 316 (1964).

107. Saville, T.
On the Nature of Color in Water
JNEWWA, 31, 78 (1917).

108. Shapiro, J.
Chemical and Biological Studies on the Yellow Organic Acids of Lake Water
J. Limnol. Oceanog., 2, 161 (1957).

109. Singley, J.E., Maulding, J.S., and Harris, R.H.
Coagulation Symposium - Pt. III. Ferric Sulfate as a Coagulant.
Wtr. Wks. and Wastes Eng., 2, #3, 52 (1965).

110. Weston, R.S.
Purification of Soft Colored Waters
ASCE Trans., 85, 492 (1922).

111. Weston, R.S.
Decolorization of Soft, Colored Water
JAWWA, 19, 416 (1928).

112. Wilson, A.L.
Determination of Fulvic Acids in Water
J. Appl. Chem., 9, 501 (1959).

113. Wilson, A.L.
The Removal of Fulvic Acids by Water Treatment Plant
J. Appl. Chem., 10, 377 (1960).

FLOCCULATION AND COAGULATION AIDS

114. Andrews, R.V.
Continuous Production of Activated Silica with Carbon Dioxide
JAWWA, 46, 82 (1954).

115. Andrews, R.V. and Burdett, J.W.
Continuous Production of Activated Silica with Low-CO_2 Gases
JAWWA, 48, 713 (1956).

116. Baylis, J.R.
Bleaching Clays
Wat. Wks. and Sew., 80, 287, (1933).
C.A., 28:1433 (1934).

117. Baylis, J.R.
Silicates as Aids to Coagulation
JAWWA, 29, 1355 (1937).

118. Baylis, J.R. and Mrva, A.E.
Use of Acid-Treated Sodium Silicate in Coagulation
JAWWA, 55, 1536 (1963).

119. Black, A.P., Ball, A.I., Black, A.L., Boudet, R.A., and Campbell, T.N.
Effectiveness of Polyelectrolyte Coagulant Aids in Turbidity Removal
JAWWA, 51, 247 (1959).

120. Black, A.P., Birkner, F.B. and Morgan, J.J.
Destabilization of Dilute Clay Suspensions with Labeled Polymers
JAWWA, 57, 1547 (1965).

121. Black, C.A.
Activation of Silica for Use in Water Treatment
JAWWA, 45, 1101 (1953).

122. Cohen, J.M., Rourke, G.A. and Woodward, R.L.
Natural and Synthetic Polyelectrolytes as Coagulant Aids
JAWWA, 50, 463 (1958).

123. Conley, W.R. and Pitman, R.W.
Innovations in Water Clarification
JAWWA, 52, 1319 (1960).

124. Conway, B.E.
Natural and Synthetic Polyelectrolytes
Discovery, 16, 378 (1955).

125. Graf, A.V. and Schworm, W.B.
Solution Mixture of Sodium Silicates Improve Coagulation
Wat. Wks. Engng., 90, 1514 (1937).

126. Griffin, A.E.
Preparation and Use of Activated Silica
JAWWA, 46, 571 (1954).

127. Griffin, A.E. and Baker, R.J.
Aids for Water Conditioning
Munic. Util. 95: No. 7, 54 (1957).

128. Hall, R.I.
A Works Evaluation of Sodium Alginate as a Coagulant Aid
Proc. Soc. Water Treat. and Exam., 13, 114 (1964).

129. Hay, H.R.
Water Purification Methods Involving Sodium Silicates
JAWWA, 36, 626 (1944).

130. Healy, T.W.
Flocculation-Dispersion Behavior of Quartz in the Presence of a Polyacrylamide Flocculant
J. Colloid Sci., 16, 609 (1961).

131. Healy, T.W. and LaMer, V.K.
The Energetics of Flocculation and Redispersion by Polymers
J. Colloid Sci., 19, 323 (1964).

132. Henry, C.R.
Characteristics of Activated Silica Sols
JAWWA, 41, 551 (1949).

133. Henry, C.R.
New Method of Preparing Activated Silica Sols
JAWWA, 50, 61 (1958).

134. Hudson, H.E., Jr.
Flocculation and Flocculation Aids
JAWWA, 49, 242 (1957).

135. Hurd, C.B.
Theories for the Mechanism of the Setting of Silicic Acid Gels
Chem. Rev., 22, 403 (1938).

136. Hyndshaw, A.Y.
Coagulation Symposium VI. Activated Carbon in the Coagulation Process.
Wtr. Wks. and Wastes Eng., 2, #7, 58 (1965).

137. Johnson, C.E.
Polyelectrolytes as Coagulants and Coagulation Aids
Ind. Eng. Chem., 48, 1080 (1956).

138. Kane, J.C., LaMer, V.K. and Linford, H.B.
The Filtration of Silica Dispersions Flocculated by High Polymers
J. Phys. Chem., 67, 1977 (1963).

139. Klinger, L.L.
Experience with Activated Silica
JAWWA, 47, 175 (1955).

140. Kragh, A.M. and Langston, W.B.
The Flocculation of Quartz and Other Suspensions with Gelatine
J. Colloid Sci., 17, 101 (1962).

141. LaMer, V.K. and Healey, T.W.
Adsorption-Flocculation Reactions of Macromolecules at the Solids-Liquid Interface
Rev. Pure and Applied Chem., 13, 112 (1963).

142. LaMer, V.K. and Smellie, R.H.
Flocculation, Subsidence and Filtration of Phosphate Slimes. I. General
J. Colloid Sci., 11, 704 (1956).

143. LaMer, V.K and Smellie, R.H.
Flocculation Subsidence and Filtration of Phosphate Slimes. II. Starches as Agents for Improving Flocculation, Subsidence and Filtration
J. Colloid Sci., 11, 710 (1956).

144. LaMer, V.K. and Smellie, R.H.
Theory of Flocculation, Subsidence and Refiltration Rates of Colloidal Dispersions Flocculated by Polyelectrolytes
Clay and Clay Minerals, 9, p. 295, Pergamon Press, London (1962).

145. LaMer, V.K., Smellie, R.H., and Lee, P.K.
Flocculation, Subsidence, and Filtration of Phosphate Slimes. IV. Flocculation by Gums and Polyelectrolytes and their Influence on Filtration Rate.
J. Colloid Sci., 12, 230 (1957).

146. Langworthy, V.W.
Use of Alum-Activated Silica as a Coagulant Aid
JAWWA, 50, 56 (1958).

147. Lordley, H.E. and Smith, M.C.
Studies in the Use of Sodium Silicate
JAWWA, 31, 2149 (1939).

148. Michaels, A.S.
Aggregation of Suspensions by Polyelectrolytes
Ind. Eng. Chem., 46, 1485 (1954).

149. Michaels, A.S. and Morelos, O.
Polyelectrolyte Adsorption by Kaolinite
Ind. Eng. Chem., 47, 1801 (1955).

150. Minz, D.M.
Aids to Coagulation - General Report No. 5
International Water Supply Congress, Stockholm, Sweden, June (1964).

151. Mueller, K.C. and Burbank, N.C. Jr.
Effects of Polyelectrolyte Coagulant Aids on Removal of Missouri River Turbidity with Ferric Sulfate
JAWWA, 56, 333 (1964).

152. Norcom, G.D.
Bleaching Clay in Water Purification
Wat. Wks. & Sewerage, 80, 53 (1933).

153. Olin, H.L. and Gauler, J.V.
The Use of Bentonite Clays in Water Treatment
JAWWA, 30, 498 (1938).

154. Olin, H.L. and Peterson, M.H.
The Use of Bentonite as a Coagulant in Water Treatment
JAWWA, 29, 513 (1937).

155. Palin, A.T.
Controlled Filter Breakthrough by the Addition of Activated Silica to Settled Water
Water and Water Engineering, 63, 258 (1959).

156. Rew, M.E.
Use of Sodium Aluminate as a Coagulant at Council Bluffs
JAWWA, 52, 852 (1960).

157. Ruehrwein, R.A. and Ward, D.W.
Mechanism of Clay Aggregation by Polyelectrolytes
Soil Sci., 73, 485 (1952).

158. Schaffer, R.B.
Polyelectrolytes in Industrial Waste Treatment
Ind. Wat. and Wastes, 8, #6, 34 (1963).

159. Slocum, E.
Bleaching Clay in Water Purification
Public Works, 63, 11 (1932).

160. Spaulding, C.H., Lowe, H.N., and Schmitt, R.P.
Improved Coagulation by the Use of Pulverized Limestone
JAWWA, 43, 793 (1951).

161. Stuart, F.E.
Powdered Activated Carbon in Water Purification
JNEWWA, 46, 312 (1932).

162. Tenney, M.W. and Stumm, W.
Chemical Flocculation of Microorganisms in Biological Waste Treatment
J. Wat. Poll. Cont. Fed., 37, 1370 (1965).

163. Vail, J.G.
Soluble Silicates. Their Properties and Uses, Vols. 1 and 2
Reinhold Publ. Co., New York (1952).

164. Walker, J.G.
Activated Silica. Its Laboratory Preparation and Evaluation in Water Treatment Processes
Wat. & Wat. Engng., 59, 534 (1955).

165. Weston, R. S.
The Use of Chlorine to Assist Coagulation
JAWWA, 11, 446 (1924).

166. Wheaton, H.J. and Walker, J.G.
Activated Silica as an Aid to Coagulation
Chem. & Ind., 1950, 710-16, 802-5.

167. Whitlock, E.A.
The Chlorine Activation of Silica
Proc. Soc. Wat. Treat. and Exam., 3, 49 (1954).

168. Wright, R.E.
Coagulation Symposium IV. Activated Silica as a Coagulant Aid
Wtr. Wks. & Wastes Eng., 2, #4, 60 (1965).

DOSAGE AND PROCESS CONTROL

169. Anon.
Coagulation Control Tests. Jar Test Procedures.
Water & Sew. Wks. Ref. & Data Ed., 102, No. 6, R-97 (1955).

170 Babcock, R.H. and Knowlton, K.F.
Conductivity-Difference Control of Chemical Coagulation
JAWWA, 48, 622 (1956).

171. Baker, R.A., Campbell, S.J., and Anspach, F.R.
Electrophoretic and Taste and Odor Measurement in Plant Control
JAWWA, 57, 363 (1965).

172. Baylis , J.R.
Sensitive Detection of Suspended Matter
Public Works, 52, 6 (1922).

173. Baylis, J.R.
Measuring the Volume of Coagulated Matter Passing Filter Beds
Water Works & Sewerage, 78, 33 (1931).

174. Bean, E.L., Campbell, S.J., and Anspach, F.R.
Zeta Potential Measurements in the Control of Coagulation Chemical Dosage
JAWWA, 56, 214 (1964).

175. Black, A.P., Buswell, A.M., Eidsness, F.A., and Black, A.L.
Review of the Jar Test
JAWWA, 49, 1414 (1957).

176. Black, A.P. and Hannah, S.A.
Measurement of Low Turbidities
JAWWA, 57, 901 (1965).

177. Black, A.P. and Smith A.L.
Determination of the Mobility of Colloidal Particles by Microelectrophoresis
JAWWA, 54, 926 (1962).

178. Black, A.P. and Smith, A.L.
Improvements in Instrumentation and Techniques for Microelectrophoresis
JAWWA, 57, 485 (1965).

179. Black, A.P. and Smith, A.L.
Suggested Method for Calibration of Briggs Microelectrophoresis Cells
JAWWA, 58, 445 (1966).

180. Buswell, A.M.
Method for Automatic Control of Coagulant Dosage
JAWWA, 50, 479 (1958).

181. Buswell, A.M. and Larson, T.E.
Optical Difficulties with the Cylindrical Cataphoresis Cell
J. Phys. Chem., 40, 833 (1936).

182. Coffman, P.A., Jr.
Automation and Remote Control of Chemical Feeders
JAWWA, 49, 1378 (1957).

183. Cohen, J.M.
Improved Jar Test Procedure
JAWWA, 49, 1425 (1957).

184. Conley, W.R., Jr.
Integration of the Clarification Process
JAWWA, 57, 1333 (1965).

185. Flentje, M.E. and Wilson, P.S.
Efficient Water Works Operation and the Purification Laboratory
JAWWA, 23, 7 (1931).

186. Granstrom M. and Shearer, S.D.
Conductometric Control of Coagulant Dosage in Treatment Plants
JAWWA, 50, 410 (1958).

187. Hall, E.S.
The Zeta Potential of Aluminum Hydroxide in Relation to Water Treatment Coagulation
J. Appl. Chem., 15, 197 (1965).

188. Hopkins, E.S.
Coagulation Control with a Recording Potentiometer
JAWWA, 27, 94 (1935).

189. Kawamura, S. and Tanaka, Y.
Applying Colloid Titration Techniques to Coagulant Dosage Control
Wtr. and Sew. Wks., 113, 348 (1966).

190. Knight, A.G.
The Measurement of Turbidity in Water
J. Inst. Water Engrs., 4, 449 (1950).

191. Liepold, C.
Mechanical Agitation and Alum Floc Formation
JAWWA, 26, 1070 (1934).

192. Nickel, J.B.
Fundamental Techniques for Running Jar Tests
JAWWA, 37, 1207 (1945).

193. Ockershausen, R.W.
Coagulation Symposium, Pt. 1. Process Control in Plants Using Aluminum Sulfate.
Wtr. Wks. and Wastes Eng., 2, #1, 53 (1965).

194. Packham, R.F.
The Absorptiometric Determination of Aluminum in Water
Proc. Soc. Wat. Treat. and Exam., 7, 102 (1958).

195. Packham, R.F.
A Multiple Stirrer Unit for Coagulation Tests
Wat. & Wat. Eng., 66, 105 (1962).

196. Palin, A.T.
Photometric Determination of Color and Turbidity of Water
Water and Sew. Works, 104, 492 (1957).

197. Riddick, T.M.
A Stirring Apparatus for the Determination of Coagulant Doses
Water Works and Sewerage, 81, 358 (1934).

198. Riddick, T.M.
Zeta Potential: New Tool for Water Treatment Pt. I.
Chem. Eng., 68, 13:121 (1961).
Pt. II, Chem. Eng., 68, 14:141 (1961).

199. Riddick, T.M.
Zeta Potential and its Application to Difficult Waters
JAWWA, 53, 1007 (1961).

200. Riddick, T.M.
Role of Zeta Potential in Coagulation Involving Hydrous Oxides
Tappi, 47, 171A (1964).

201. Rock, R.M. and Burbank, N.C., Jr.
Improved Briggs Microelectrophoresis Cell and Comparisons with the Riddick Cell
JAWWA, 58, 676 (1966).

202. Rose, H.E.
The Analysis of Water by the Assessment of Turbidity
J. Inst. Water Engrs., 5, 521 (1951).

203. Tolman, S.L.
Use of Models in Solving Flocculation Problems
JAWWA, 41, 641 (1949).

204. Vaughn, J.C.
Coagulation Symposium V. Inplant Evaluation and Control of Coagulation is One Tool for Better Service
Wtr. Wks. & Wastes Eng., 2, #6, 100 (1965).

205. Williams, R.L.
Microelectrophoretic Studies of Coagulation with Aluminum Sulfate
JAWWA, 57, 801 (1965).

206. Woxholt, W.G.
Electrical Conductivity and the Stability of Colloids
JAWWA, 51, 885 (1959).

METAL COAGULANTS

207. Beal, R.B. and Stevens, S.
Sodium Aluminate in Modern Water Treatment
J. Soc. Chem. Ind., 50, 307 (1931).

208. Besselievre, E.B.
Economics of Coagulants. Parts I-IV.
Wat. Wks. and Wastes Eng., 1, No. 10, 39 (1964); 1, No. 11, 57 (1964); 1, No. 12, 49 (1964); 2, No. 1, 59 (1965).

209. Black, A.P., Bardwell, R.A., and Graham, B.W.
Coagulation as Applied to Industrial Waters
JAWWA, 29, 1533 (1937).

210. Burke, J.T.
Sodium Aluminate in Water Clarification and Softening
Wat. Wks. and Wastes Eng., 2, No. 2, 64 (1965).

211. Clark, L.M. and Price, L.S.
The Role of Sodium Aluminate in Accelerating the Separation of Solid Phases During Water Softening Operations
J. Soc. Chem. Ind., 52:35T (1933).

212. Clark, R.N.
Water Coagulation with Ferric Chloride
Public Works, 64, 22 (1933).

213. Gullans, O.
Techniques in the Use of Liquid Alum
JAWWA, 49, 1322 (1957).

214. Hedgepeth, L.L.
Coagulants Used in Water Purification and Why
JAWWA, 26, 1222 (1934).

215. Hedgepeth, L.L. and Olsen, W.C.
Chlorinated Copperas - A New Coagulant
JAWWA, 20, 467 (1928).

216. Hopkins, E.S. and Whitmore, E.R.
Study of Floc Produced by Chlorinated Copperas
Ind. Eng. Chem., 22, 79 (1930).

217. Hyde, C.G.
Practical Aspects of Coagulation with Ferric Chloride
JAWWA, 27, 631 (1955).

218. Nickel, J.B.
Coagulation with Ferric Sulfate
JAWWA, 38, 755 (1946).

219. Nolte, A.G. and Kramer, W.A.
Floc Formation Studies in Water Purification
Ind. Eng. Chem., 25, 1110 (1933).

220. Ockershausen, R.W.
Techniques in the Use of Liquid Alum
JAWWA, 49, 1315 (1957).

221. Ockershausen, R.W.
Use of Liquid Alum in Water Plants
JAWWA, 57, 309 (1965).

222. Powell, S.T.
Sodium Aluminate, an Adjunct to Coagulation
Am. J. Pub. Health, 17, 804 (1927).

223. Ridley, C.N.
Sodium Aluminate as an Adjunct to Lime Soda Feed Water Treatment
Steam Eng., 3, 127 (1933).

224. Schworm, W.B.
Iron Salts for Water and Waste Treatment
Public Works, 94, #10, 118 (1963).

225. Vaughn, J.C.
Common Chemicals Used in Coagulation
Wtr. & Sew. Wks. Reference Number, Vol. 108, p. R-207 (1961).

GENERAL REFERENCES

226. Anon.
Betz Handbook of Industrial Water Conditioning. 6th Ed.
Betz Laboratories Inc., Philadelphia. Pa. (1962).

227. Camp, T.R.
Water and Its Impurities
Reinhold Publishing Corp., New York, N.Y. (1963).

228. Cox, C.R.
Operation and Control of Water Treatment Processes
World Health Organization, Geneva (1964).

229. Fair, G.M. and Geyer, J.C.
Water Supply and Waste-Water Disposal
John Wiley & Sons, Inc., New York (1954).

230. Hardenbergh, W.A.
Water Supply and Purification.3rd Ed.
International Textbook Company, Scranton, Pa. (1952).

231. Hirsch, A.A.
Manual for Water Plant Operators
Chemical Publishing Co., Inc., New York, N.Y. (1945).

232. Hopkins, E.S. and Bean, E.L.
Water Purification Control
The Williams and Wilkins Co., Baltimore, Md. (1966).

233. James, B.V.
Water Treatment
3rd Ed. London, Technical Press (1965).

234. Nordell, E.
Water Treatment for Industrial and Other Uses. 2nd Ed.
Reinhold Publishing Corp. New York City (1961).

235. Powell, S.T.
Water Conditioning for Industry
McGraw-Hill Book Co. Inc., New York City (1954).

236. Riehl, M.L.
Hoover's Water Supply and Treatment. 8th Ed. Bulletin 211.
Natl. Lime Assoc., Washington 5, D.C. (1957).

237. Sawyer, C.N.
Chemistry for Sanitary Engineers
McGraw-Hill Book Company, Inc., New York, N.Y. (1960).

ADDENDUM TO

Selected Bibliography

on

COAGULATION AND FLOCCULATION

The original bibliography includes references through 1965. Several more recent references have been selected and are segregated in the same manner as in the original.

Recent references regarding the use of polyelectrolytes in flocculation and coagulation are included in the sections on flocculation and coagulation aids.

Other aspects and uses of polyelectrolytes in water treatment included in the last category. The categories are as follows:

Theory and Mechanism of Coagulation

Coagulation in Water Treatment

Factors Influencing Coagulation

Coagulation of Color

Flocculation and Coagulation Aids

Dosage and Process Control

General References

Special Polyelectrolyte References

- Primary Coagulant
- Filter Aid
- Backwash Aid
- Sludge Conditioner
- Public Health Aspects

THEORY AND MECHANISM OF COAGULATION

1. Camp, Thomas R.
Floc Volume Concentration
JAWWA, 60, 656-73, (1968).

2. Harris, Howard S.; Kaufman, Warren J.; Krone, Ray B.
Ortho Kinetic Flocculation in Water Purification
J. Sanit. Eng. Div. Proc. Amer. Soc. Civil Eng. 92, SA6, 95-113
(Dec. 1966).

3. Lange, K. R. and Spences, R. W.
The Mechanism of Silica Sol as a Coagulant Aid.
Amer. Chem. Soc., Div. Water Waste Chem., Preprints 7,
155-63 (1967).

4. Singley, J. Edward; Birkner, Frank; Chen, Ching-Lin;
Cohen, Jesse H., et. al.
State of the Art of Coagulation
JAWWA 63, 99-108, (1971).

5. Stumm, Werner and O'Melia, Charles R.
Stoichiometry of Coagulation
JAWWA 60, 514-39, (1968).

COAGULATION IN WATER TREATMENT

6. Hudson, H. E., Jr.
Coagulation and Flocculation of Surface Waters.
N. Engl. Water Works Assoc., 80. 232-52 (1966).

7. Hyndshaw, A. W.
Activated Carbon-Its Relation to Coagulation.
Amer. Chem. Soc. Div. Water Waste Chem. Preprints
4, 94-102 (1964).

8. Jorden, Roger M.
Coagulation-Flocculation
Water Sewage Works, 118, 23-25 (1971).

9. Kleber, John P.
Field Use of a Cationic Polymer for Clarification
Water Wastes Eng. 6, 42-44 (1969).

10. Middleton, A. B.
The Role of Activated Silica in Coagulation.
Am. Chem. Soc., Div. Water Waste Chem. Preprints 4, 112-17 (1964).

11. O'Melia, Chas. R.
Review of the Coagulation Process.
Publ Works, 100, 87-98, (1969).

12. Riddick, T. M.
Zeta Potential and Polymers.
JAWWA 58, 719-722 (1966).

13. Walker, J. D.
High Energy Flocculation and Air and Water Backwashing.
JAWWA 60, 321-30, (1968).

14. Yao, K. M.
Particle Aggregation in Water Pretreatment.
Water Sewage Works, 114, 295-98 (1967).

FACTORS INFLUENCING COAGULATION

15. Ham, Robt, K. and Christman, Russell F.
Agglomerate Size Changes in Coagulation.
J. Sanit. Eng. Div., Amer. Soc. Civil Eng. 95, 481-502, (1969).

16. Hannah, George P. Jr. and Rubin, Alan C.
Effect of Sulfate and Other Ions in Coagulation with Aluminum (III).
JAWWA 62 (5), 315-21, (1970).

17. Letterman, Raymond D.; Quon, J. E.; Gemmell, Robt. S.
Coagulation of Activated Carbon Suspensions.
JAWWA, 62 (10), 652-58 (1970).

18. Maulding, Jeanette S. and Harris, Robt. H.
Effect of Ionic Environment and Temperature on the Coagulation of Color Causing Organic Compounds with Ferric Sulfate.
JAWWA 60, 460-76, (1968).

19. Miller, D. G. and West, J. T.
Floc Blanket Clarification. II. Effect of Chemical Variables on Floc Blanket Behavior Using $Al_2(SO_4)_3$ as Coagulant.
Water Wastes Eng. 70, 291-94, (1966).

20. Miller, D. G. and West, J. T.
Floc Blanket Clarification, III.
Water Wastes Eng. 70, 342-46 (1966).

COAGULATION ON COLOR

21. AWWA Research Committee Report
Coagulation and Color Problems.
JAWWA, 62, 311-14, (1970).

22. Kawamura, Susumu
Removal of Color by Alum Coagulation I.
Water Sewage Works 114, 282-85 (1967).

23. Sankey, K. A.
The Problem of Sludge Disposal at the Arnfield Treatment Plant.
J. Inst. Water Eng. 21, 367-84 (1967).

24. Kawamura, Susumu
Removal of Color by Alum Coagulation II.
Water Sewage Works 114, 324-27 (1967).

FLOCCULATION AND COAGULATION AIDS

25. Ballance, Richard C.; Capp, John P.; Burchinal, Jerry C.
Fly Ash as a Coagulant Aid in Water Treatment
U. S. Dept. Interior, Bur. Mines Rep. Invest. No. 6869, 13 pp (1966).

26. Birkner, Francis B. and Edzwald, J. K.
Nonionic Polymer Flocculation of Dilute Clay Suspension.
JAWWA 61, 645-51, (1969).

27. Black, Alvin Percy and Vilaret, Manuel R.
Effect of Particle Size on Turbidity Removal.
JAWWA 61, 209-14, (1969).

28. Bond, A. W.
Water Solids Separation in an Upflow. The Use of a Slurry Pool for Solids Contact in Water Treatment.
J. Inst. Water Eng. 2, 477-89 (1966).

29. Carr, Ralph L., Jr.
Polyelectrolytes Coagulant Aids, Dry and Liquid, Handling and Application
Water Sewage Works 114, 64-72, (1967).

30. Grieves, Robt. B. and Crandall, Clifford J.
Water Clarification by Foam Separation: Bentonite as a Flotation Aid.
Water Sewage Works, 113, 432-37 (1966).

31. Hawkes, Barbara E.
Polyelectrolytes in Water Treatment.
J. N. Engl. Water Works Assoc. 84, 189-213, (1970).

32. La Mer, Victor K.
Coagulation vs. the Flocculation of Colloidal Dispersions by High Polymers (Polyelectrolytes).
Principles Appl. Water Chem., Proc. Rudolfs Res. Conf. 4th, Rutgers St. Univ., 246-73, 1965 (Pub. 1967).

33. Pressman, M.
Clarification of Potomac River Water with Cationic Polyelectrolytes.
U.S. Dept. Comm. AD 634633, 15 pp (1966).

34. Sexsmith, David R.; Savinelli, E. A.; Beecher, J.S.
Use of Polymers for Water Treatment.
Ind. Water Eng. 6, 18-23, (1969).

35. Tilton, R. C.; Murphy, John; Dixon, J. K.
Control of the Algal Content of Water With Synthetic Polymeric Flocculant.
Amer. Chem. Soc., Div. Water, Air, Waste Chem., 9, 102-107, (1969).

DOSAGE AND PROCESS CONTROL

36. Bean, E. L.
In-Plant Electrophoretic Evaluation and Control of Coagulation Process.
Amer. Chem. Soc.,Div. Water Waste Chem. Preprints 4, 76-81 (1964).

37. Bean, E. L.; Campbell, S. J.; Anspach, F. R.
Coagulation Symposium X, —Electrophoretic Coagulation and Process Control.
Water Works Waste Eng. 2, 47-50, (1965).

38. Bernhardt, H.; Clasen, J.; Schell, H.
Phosphate and Turbidity Control by Flocculation and Filtration
JAWWA, 63 (6), 355-68 (1971).

39. Derek, G. Miller and West, John T.
Pilot Plant Studies of Floc Blanket Clarification.
JAWWA 60, 154-64 (1968)

40. Hemenway, David R. and Keshavan, K.
Determination of Optimun Velocity Gradients for Waters Coagulated w̄ Polyelectrolytes.
Water and Sewage Works, 115, 554-59 (1968)

41. Kawamura, Susumu and Hanna, G. P.
Coagulation Dosage Control by Colloid Titration Technique.
Purdue Univ. Eng. Bull., Ext. Ser., No. 121, 381-402 (1966).

42. Kawamura, Susumu; Hanna, G. P., Jr.; Shumate, K. S.
Application of Colloid Titration Technique to Flocculation Control
JAWWA 59, 1003-13 (1967).

43. TeKippe, Rudy J. and Ham, Robt. K.
Coagulation Testing: A Comparison of Techniques
JAWWA 62 (9), 594-602, (1970).

44. Vrale, Lasse and Jorden, Roger M.
Rapid Mixing in Water Treatment.
JAWWA 63, 52-58 (1971).

GENERAL REFERENCES

45. Water Quality and Treatment: A Handbook of Public Water Supplies. 3rd ed.
American Water Works Association, Inc., New York, 646 pp (1971).

46. Behrman, Abraham S.
Water is Everybody's Business: The Chemistry of Water Purification.
Anchor Books, N.Y. (1968).

47. Eckenfelder, W. Wesley, Jr. - Editor
Manual of Treatment Processes Water Resource Management Series.
Environmental Sci. Serv. Corp., Stamford, Connecticut (1968)

48. Fair, G. M. and Geyer, J. C.
Waste and Wastewater Eng. Vol. 2: Water Purification and Wastewater Treatment and Disposal.
Wiley: N. Y. (1968).

49. Fair, Gordon M.; Geyer, John Charles; Okun, Daniel Alexander
Water Supply and Waste Water Removal.
Water and Wastewater Engineering Vol. 1, Wiley: N. Y. (1966).

SPECIAL POLYELECTROLYTE REFERENCES

Primary Coagulant

50. Pressman, M.
Cationic Polyelectrolytes as Prime Coagulants in Natural Water Treatment.
JAWWA 59, 169-82 (1967).

Filter Aid

51. Dillingham, J. H.; Cleasby, J. L.; Bauman, E. R.
Optimum Design and Operation of Diatomite Filtration Plants.
JAWWA 58, 657-72 (1966).

52. Geise, G. D.; Pitman, R. W.; Wells, G. W.
Filter Conditioners in Water Treatment.
JAWWA 59, 1303-09 (1967).

Backwash Aid

53. Oulman, Chas. S. and Bauman, E. R.
Polyelectrolyte Coatings for Filter Media.
Ind. Water Eng., 8 (5), 22-25 (1971).

Sludge Conditioner

54. Bugg, Henry M.; King, Paul Hamilton; Randall, Clifford W.
Polyelectrolyte Conditioning of Alum Sludges.
JAWWA 62, 792-795, (1970).

55. Hollo, Ja'nos
Treatment of Water and Sludge.
Aust. Chem. Eng. 10, 19-24, (1969), (England).

56. Neubauer, W. K.
Waste Alum Sludge Treatment.
JAWWA, 60, 819-26, (1968).

57. Sankey, K. A.
The Problem of Sludge Disposal at the Arnfield Treatment Plant.
(Manchester Corporation Waterworks).
J. Inst. Water Eng. 21, 367-84 (1967).

Public Health Aspects

58. Coagulant Aids for Water Treatment-EPA
Report
JAWWA 63, 388-99, (1971)

59. Thorup, Robt. T.; Nixon, F. Patrick; Wentworth, David F.;
Sproul, Otis J.
Virus Removal by Coagulation w̄ Polyelectrolytes.
JAWWA 62, 97-101, (1970).